"In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institution shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

"

METHODS FOR THE DETERMINATION OF RADON-222, RADIUM-226, AND LEAD-210 IN WATER

A THESIS

Presented to

the Faculty of the Graduate Division

by

Frederick Benjamin Higgins, Jr.

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Sanitary Engineering

Georgia Institute of Technology

June, 1960

METHODS FOR THE DETERMINATION OF

RADON-222, RADIUM-226, AND LEAD-210 IN WATER

Approved

Dr. W. N. Grüne

R. E. Stiemke

Dr. R. H. Fetner

Date Approved by Chairman May 12, 1960

ACKNOWLEDGMENTS

There is no adequate expression of gratitude for the advice and support which Dr. Werner N. Grune has given to the studies for this thesis. Many individuals have played an important role in these investigations, too many to be able to list them all.

To Dr. and Mrs. Charles D. Brown and their son Jeffrey go much of the credit, for without their hospitality such an undertaking would have been impossible. Mr. and Mrs. Stewart D. Hodgdon also deserve much appreciation for their hospitality.

To Mr. and Mrs. Benjamin M. Smith, Mr. Roy C. Peek, Jr., and Mrs. Nancy Jane Higgins go thanks for aid in the laboratory. In addition, the help of Messrs. J. G. Lee and J. M. Mehaffy should be acknowledged for their contributions in detection instrumentation.

Financial aid and assistance were received from the Division of Radiological Health of the United States Public Health Service, the Division of Sanitary Engineering of the Department of Health and Welfare of the State of Maine, the Water Pollution Commission of New Hampshire, and from a Public Health Traineeship.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SUMMARY

The purpose of this study was to develop a simple, reliable, and reproducible method for the analysis of certain of the naturally occurring radioisotopes in water. The procedures were to be applied to the analysis of water supplies, particularily ground waters, during a relatively extensive field sampling program. The requirements, therefore, differed from those of many existing analytical methods in that equipment had to be compact and portable. In order to achieve significant results during a limited and expensive field survey, it was desirable that the analytical procedures be as rapid as possible without loss of accuracy.

Three analytical approaches were investigated in the solution of the problem. The first of these involved the precipitation of radon-222 daughters, as sulfides, with subsequent separation on a millipore filter for analysis by alpha counting. Difficulty was encountered when using this procedure because of clogging of the millipore paper during the filtration of a number of samples. The clogging appeared to result from the presence of an unknown, pinkish-brown substance which could not be removed by filtration before precipitation. As a part of this investigation, a sample was filtered twice without addition of reagents. Radon daughter recovery was low as determined by comparison with the known

alpha activity of the sample and by the relatively large alpha activity retained on the second filter.

A second analytical procedure studied involved the de-emanation of radon-222 from solution, collection of the gases in an Erlenmeyer flask coated with a powdered, silver-activated zinc sulfide screen, followed by alpha scintillation counting. Water samples were collected in specially designed glass bubblers. De-emanation was achieved by means of an evacuated Erlenmeyer flask connected to a bubbler. The vacuum was used to produce an upward flow of air through the bubbler and resulted in radon removal from the water and collection in the flask. The analysis was completed by alpha scintillation counting of the flask, using a specially designed detection unit.

Radium-226 was also analyzed using a simple modification of the de-emanation procedure. After de-emanation for radon analysis, the water sample was thoroughly purged of any remaining radon. The bubbler was then sealed for from 8 to 12 days to allow the build-up of radon from the radium in the sample. A second radon analysis was performed on the sample; and the radium content was calculated using the known state of partial equilibrium between the two radio-elements.

The results of the investigation of the de-emanation procedure are listed below:

1. The precipitation, as sulfides, of the lead,

bismuth, and polonium daughters of radon-222, with subsequent collection on a millipore filter, produced poor results on certain well waters from Raymond, Maine, because of clogging of the filter paper produced by an unknown precipitate.

2. Verification of radon-222 as the responsible radioisotope was obtained by the repeated counting of four samples from two wells. The experimentally determined half-life of 3.80 days compares favorably with the accepted value of 3.825 days.

3. The efficiency of radon removal from bubblers, by de-emanation, averaged 99.3 per cent when Corning Glass Works' components were used in bubbler construction. The removal efficiency of a second group of bubblers assembled of components produced by Consolidated Glass Works averaged 89.6 per cent. Removal efficiencies were determined with standard radium solutions in the Corning bubblers, while water samples were used in the others for routine determinations only.

4. The alpha counting efficiency of the scintillation detector varied with time due to the photomultiplier tube decay, necessitating frequent measurements and the use of corrections obtained from a graph of counting efficiency versus time.

5. The de-emanation method of radon analysis was reproducible on samples to within $\pm$ 9.19 per cent, at 95 per cent confidence, when the time interval between sampling was short.

6. The radon content of a well was found to vary with time within a 95 per cent confidence interval of ± 14.0 per cent; thus, the reproducibility of the method was reduced as determined by successive samples from a single source.

The third analytical procedure was for the determination of both radon-222 and lead-210. This method employed solvent extraction of lead and bismuth from water. The extracting agent was diphenylthiocarbazone, commonly used in the colorimetric analysis of heavy metals, dissolved in chloroform. After separation of the radon daughters, the lead and bismuth dithizonates were deposited by evaporation of the chloroform on a planchet. The radon concentration was determined by an alpha count of the planchet and through the use of the theoretical daughter decay relationships. Lead-210 was determined by waiting for the short-lived daughters to decay before recounting for the beta activity. The results were inconclusive because of non-uniform deposition of solids on the planchet.

INTRODUCTION

General

The evaluation of human exposure to naturally occurring radioactivity has only become of public health importance in the last few years, although the existence of natural activity has been known for more than 100 years. With the increased concern over the problems of radioactive fallout and the monitoring of the areas in the vicinity of nuclear reactors, extensive radiological surveys have become necessary to determine the existing types and quantities of artificial and natural radioactivities (1). In some instances, the levels of natural activity discovered have been sufficiently high to cause concern. Because of the recent attention to the problem, many of the state health departments have not had sufficient time to familiarize themselves with the special techniques required for the analysis of natural activity. Consequently, there has been a lag in the development of methods of laboratory analysis suitable to the large scale requirements of an extensive field sampling program.

With the discovery of high concentrations of radioactivity in well waters in several areas in Maine and New

Hampshire, an excellent opportunity presented itself to aid in the development of more specific and efficient methods for the analysis of natural radioactivity. A study to investigate the nature, extent, and effect on consumers of natural radioactivity in ground water supplies in Maine and New Hampshire was requested of the United States Public Health Service. The Public Health Service, in turn, requested that the Sanitary Engineering Laboratories at the Georgia Institute of Technology perform the field studies necessary for the determination of human exposure. The evaluation of the natural activity to be encountered immediately resolved itself into two distinct phases. The development of methods for the analysis of natural radioactivity is discussed herein. The second phase, the analysis of the results of the field program to delineate the occurrence and extent of natural activity, has been studied by Mr. Benjamin M. Smith (2).

Analyses of water from the Dielectric Products Engineering Company, Inc., Raymond, Maine, by two United States Public Health Service laboratories and by the Division of Sanitary Engineering of the State of Maine (3), showed quantities of radon far in excess of the equilibrium value with radium. Table 1 shows the results of these analyses along with several analyses for radium performed by the United States Geological Survey (4). In addition, approximately fifty other samples were analyzed by the State of Maine (3) and all contained high radon activities. Upon

Table 1

Radioassays of Well Waters in Maine

Source	Radon-222 + daughters ($\mu\mu$c/l)	Radium-226 ($\mu\mu$c/l)	Uranium (μgm/l)	Long-lived Alpha Activity ($\mu\mu$c/l)
R.A.Taft Sanitary Engineering Center*	583,000	---	---	520
Occupational Health Field Station*	228,000**	64	860	666
State Health Dept. of Maine*	563,410	45	---	420
U.S. Geol. Survey				
(Augusta Water Dept. Augusta)	---	<0.1	0.8	---
(T.G. Weigand, Vassalboro)	---	0.1	<0.1	---
(Sheldon S. Grant, Windham)	---	3.3	11	---
(Raymond Water Co., Raymond)	---	<0.1	0.2 $\pm$ 0.1	---
(Portland Water Supply, N. Windham)	---	0.1	1 $\pm$ 0.1	---
(Chas. Harmon, Raymond)	---	0.5 $\pm$ 0.1	34 $\pm$ 3	---
(Dielectric Prod.Eng. Co. Inc., Raymond)	---	57 $\pm$ 2	960 $\pm$ 96	---
(Portland Pipeline Co., Raymond)	---	0.1	110 $\pm$ 11	---

*Samples from Dielectric Prod. Eng. Co. Inc., Raymond

**Radon-222 only

consideration of these results, it appeared that the major portion of the activity to be encountered would probably be due to radon and its immediate daughters. Most of the previous investigations of natural radioactivity in water had been confined to the determination of radium and uranium only. However, the results of several studies showed that radon concentrations may be expected to exceed those of radium by a large factor (5) (6) (7) (8).

Emphasis was placed on the development of a method for radon analysis which would produce reliable results, but which could also be adapted to large-scale field sampling programs. As shown by the maximum permissible concentration* in drinking water, radium, which is accumulated by the body, is considered to be much more dangerous than radon. Therefore efforts were also made to determine a suitable method of radium analysis. Since most natural lead compounds are insoluable, lead-210 was not expected to be present in large concentrations. The investigation of lead-210 was an outgrowth of the studies of methods for radon analysis.

Existing Analytical Methods

A search of the literature revealed a number of existing methods for the analysis of both radon and radium. It was found, almost without exception, that these methods

---

*MPC of radium-226 is 40 $\mu\mu$c/l. MPC of radon plus daughters is 2,000 $\mu\mu$c/l (9).

were designed for the determination of low concentrations of activity on the order of 0.1 $\mu\mu$c/l.* As a result, the equipment and techniques were generally too complicated and time-consuming for practical use with a large number of samples.

Although many variations exist, the analytical methods for radon and radium described in the literature may be divided into two general techniques discussed below. These are the de-emanation of radon from solution for collection and counting, employed in both radon and radium analysis, and the precipitation of radon daughters or radium for deposition on planchets and separate analyses.

Existing de-emanation techniques and equipment were developed primarily for the determination of very low concentrations of radium and have been adapted to radon determination by changes in technique. Generally, the required equipment consists of an air-tight sample container provided with apparatus for bubbling nitrogen or argon through the sample, a purification train for the removal of carbon dioxide and water from the de-emanating gas, and a pulse or vibrating-reed ionization chamber. Hursh (6) employed nitrogen gas and a purification train consisting of an acetone-dry ice water trap and a liquid nitrogen radon trap.

---

*One $\mu\mu$c is the rate of decay of 10^{-12} gm of radium-226 or 2.22 disintegrations per minute.

The radon was flushed from the liquid nitrogen during heating and was collected in a sample bulb. The radon was transferred from the sample bulb by water displacement into an alpha ionization chamber for counting.

Rieck and Perkins (10) employed de-emanation with argon while boiling the sample and a purification train consisting of a reflux condenser, "ascarite" for the removal of carbon dioxide and magnesium perchlorate for removing water vapor. Hudgens, Benzing, Cali, Meyer, and Nelson (11) have described a similar procedure, employing nitrogen, with the addition of a column of copper turnings maintained at 500° C and the inversion of the order of "ascarite" and magnesium perchlorate.

Chemical methods for the analysis of radium in waters involve the precipitation or co-precipitation of radium and subsequent collection for radioanalysis. Jenkins and Sneddon (12) combined the techniques of Russell, Lesky, and Schubert (13) with those of Ames, Sedlet, Anderson, and Kohman (14) to produce a method which included co-precipitation with lead sulfate, resolution, co-precipitation with barium chloride, and conversion of the barium-radium chloride to the sulfate. Separation was by centrifugation and the residue was counted using alpha scintillation. A procedure described by Harley and Foti (15), for the analysis of radium in urine, had been modified by Barker and Thatcher (16) to produce a method suitable for the routine analysis of

water. The procedure included co-precipitation with barium sulfate, collection on a millipore filter, and counting. This method has been adopted for use by the U.S. Geological Survey.

Only two specific methods for the analysis of radon-222 were found in the literature. Thorburn and Healy (17) had reported a procedure for radon analysis by precipitating the radon daughters with ammonium sulfide, collecting on filter paper, and counting beta activity. A similar procedure had been described by Fresco, Hardy, and Harley (18) using hydrogen sulfide as a precipitating agent, collecting on millipore filter paper, and counting alpha activity.

It was essential in these studies that rapid analytical techniques be employed and that equipment should be portable and not easily damaged. Therefore, only the procedures of Fresco, et al (18) and Thorburn and Healy (17) were considered for possible use in radon analysis. These methods, the results of which are described in Chapter II, were evaluated during the winter and spring of 1959.

A method employing the de-emanation of radon from a radium solution contained in a special glass bubbler had been described by Holaday, Rushing, Coleman, Woolrich, Kusnetz, and Bale (19) for the standardization of air sampling equipment. Rushing (20) proposed that the equipment could be adapted to the analysis of water samples and also that certain radon daughters could be extracted from water by solvent

extraction using diphenylthiocarbazone. The investigation of these methods was begun in May, 1959. Since the field program began during the second half of July, 1959, and special equipment had to be constructed, the evaluation of the analytical methods was completed in the field. The availability of a large number of naturally radioactive well waters and the comprehensive study program provided an unusual opportunity for a thorough evaluation of the performance and limitations of the methods considered.

CHAPTER II

PRELIMINARY METHODS OF ANALYSIS

The analytical method chosen for the initial experimental work was developed by Fresco, Hardy, and Harley (18). The analysis was based on the removal of the radon daughters, polonium-218, lead-214, and bismuth-214, from solution by precipitation with hydrogen sulfide. The radon content was determined by extrapolation back to the time of separation using the theoretical decay curve shown in Fig. 1. The procedure as described by Fresco, et al, and as followed in initial studies is outlined below:

1. Collect a one-liter sample of the water and transfer to a one-liter polyethylene bottle containing 8.5 ml of concentrated hydrochloric acid, and 20 milligrams of Pb^{++} as the nitrate. Fill the bottle to the top, stopper tightly, and allow at least three hours to elapse before analysis.

2. Transfer the solution to a two-liter beaker and immediately bubble through H_2S rapidly until the precipitation is complete. Note the time of commencement of this step.

3. Immediately vacuum filter through a millipore paper with appropriate apparatus. Note the time at completion of this step.

4. Allow at least thirty minutes to elapse after the completion of step #3.

5. Measure the alpha activity and note the time.

6. Check for residual long-lived activity.

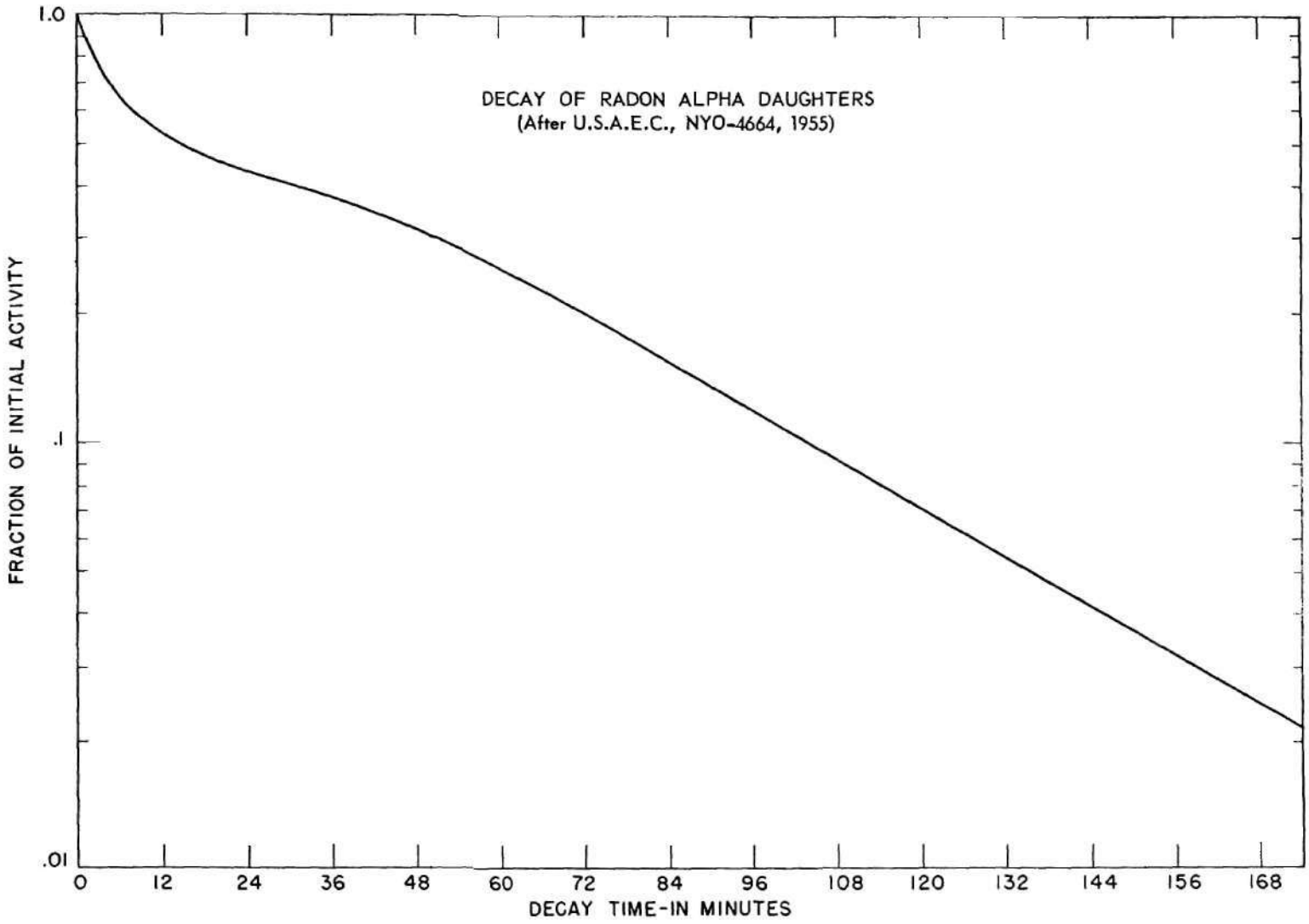


Fig. 1. Decay of Radon Alpha Daughters

The calculation of the radon activity involves the use of the follow equation:

$$\mu\mu c/l = (cpm)\left(\frac{1}{geom.}\right)\left(\frac{1}{0.8}\right)\left(\frac{1}{A/A_o}\right)\left(\frac{1}{B/B_o}\right)\left(\frac{1}{2.22}\right)\left(\frac{1}{C.D.F.}\right) \quad (1)$$

where,

cpm = alpha counts per minute corrected for background

geom. = instrument geometry

0.8 = absorption factor

A/A_o = fraction of initial daughter product activity counted

B/B_o = fraction of original radon present at the time of analysis

2.22 = disintegrations per minute per $\mu\mu c$

C.D.F. = count decay factor to correct for decay during counting.

The absorption factor listed above as 0.8 was calculated by Fresco, et al (18) experimentally and included only the self-absorption due to the PbS formed by 20 mg of Pb^{++}. The fraction of initial daughter product activity counted may be determined from Fig. 1 with the period of radon daughter product decay taken as the time difference between the midpoint of the chemical separation and the start of the activity measurement. The fraction of the original activity present at the time of analysis is a correction factor which accounts for the decay of the radon between the time of sampling and the time at the midpoint of the chemical separation. For accurate results, the additional count may be made after the

short-lived daughters have decayed to determine the contribution to the initial alpha count from any extraneous substances such as polonium-210 or radium-226.

A number of weak points were found in the above procedure. Due to the low solubility of radon in water (Henry's law constant, $K = 2.56 \times 10^{-7}$ mole fractions/mm Hg) (21), it was found to be almost impossible to contain samples in polyethylene bottles for several hours without partial radon loss. A second source of error came from the transfer of the sample from the collection bottle to the polyethylene bottle containing the reagents. Significant quantities of radon are lost unless this transfer can be accomplished without contact with air. A third source of error, reported as small, consisted of the unknown time of radon daughter isolation, taken as the midpoint of the time between the beginning of hydrogen sulfide bubbling and the completion of filtration.

To achieve complete precipitation in as short a time as possible, experiments were performed to determine whether ammonium sulfide could be used to replace hydrogen sulfide as a precipitating agent. This reagent was used by Thorburn and Healy (17) in a similar method for radon analysis. Lead sulfide crystal formation was practically instantaneous and appeared to be complete. However, the crystals were extremely small, resulting in poor carrier recoveries and long filtration times. Lead sulfide was visually detectable in the filtrate. The results of this experiment are shown in Table

9, Appendix A, page 83.

Difficulty in filtration was resolved by Thorburn and Healy through the use of Whatman No. 40 filter paper with a diatomaceous earth filtration aid. The resulting high absorption was overcome by the use of beta counting. In a brief experiment, diatomaceous earth did not significantly improve filtration time through a millipore filter. In addition, alpha counting appears to be more desirable than beta counting for radon analysis because of the lower alpha background, the higher alpha counting efficiency, and the smaller number of alpha-producing interfering radioisotopes. Consideration of the preceding factors led to the use of hydrogen sulfide in all further work.

Samples of well waters containing radon were collected in polyethylene bottles by a field party in and around Raymond, Maine, on December 24, 1958. These samples were analyzed at the Georgia Institute of Technology in accordance with the method described above with the exception of three modifications. These were: (1) the HCl and lead carrier were added to the sample in the sample collection bottle to minimize radon loss during transfer, (2) the precipitate was weighed to determine a more accurate self-absorption factor, and (3) an one-inch millipore filter was substituted for the two-inch size recommended.

Upon analysis of the first sample, it was quickly discovered that 20 mg of lead carrier were too much for

filtration through an one-inch millipore filter, since filtration times of several hours were recorded. Studies were carried out to determine the optimum amount of lead carrier by first determining the per cent recovery of various concentrations of lead from distilled water. Both lead acetate and lead nitrate were used to determine whether one of the forms of lead precipitated better than the other. The results of this study are shown in Table 10, Appendix A, page 82. Five mg/l of $Pb(NO_3)_2$ was chosen to produce the optimum combination of recovery and filtration time.

Results of the analyses of samples collected on December 24, 1958, are shown in Table 2. It may be seen that they are not compatible with the radon concentration values reported by the State Health Department of Maine. This difference is due to the error introduced by the time lapse (one to two months) between sample collection and analysis. Because of the period elapsed, the radon concentration decayed essentially to that in equilibrium with radium. Thus, extrapolation back to the time of collection on the basis of the radon half-life produced apparent radon concentrations that differed widely from (and probably are independent of) their true values. The reported activity of radon (see Table 2, column 3), at the time of analysis is, therefore, an approximation of the concentration of radium-226 (plus any interfering polonium-210). The effect of radon loss through contact with air is shown by the triplicate analyses of water

Table 2

Results of Preliminary Analyses of Maine Waters

by the H_2S Precipitation Method

(1) Source of Sample	(2) Volume of Sample (mls)	(3) Activity of Radon at Time of Pb++ Addition ($\mu\mu$c/l)	(4) Radon Activity at Time of Sampling ($\mu\mu$c/l)	(5) Activity of Radon + Dghtrs. (Maine State Health Dept.) ($\mu\mu$c/l)
B.A.Mann	200	121	18,000	66,000
B.A.Mann	1,000	92.8	4,050	66,000
Portland Pipeline Corp.				
Supt.Cot.	979	65.0*	3,700	53,760
Pump. Sta.	256	516*	7.89×10^6	5,376
Pump. Sta.	340	46.3*	2.25×10^6	5,376
Pump. Sta.	670	22.2*	0.666×10^6	5,376
L.H.Bradway Lumber Co.	501	19.1	1.39×10^6	47,500
Dielectric Products Engr. Co., Inc.	970	624	38.8×10^6	570,000

*Pink Precipitate

from the Portland Pipeline Company's Superintendent's cottage. Three samples were poured from the same bottle at intervals of about one hour. The radon content of the second sample was only about one-tenth of the first, and the third was only about one-half of the second.

A second group of samples was obtained from the State Health Department of Maine. These samples were shipped in plastic bags with tight-fitting screw caps which were expected to show a smaller loss of radon during shipment than the polyethylene bottles used previously. Reagents were also put into the bags before shipment to Maine, so that the step requiring sample transfer could be eliminated, thus reducing possible radon loss.

Upon receipt, the samples were analyzed using five mg/l of lead nitrate carrier. It was decided that filtration time would be controlled by analyzing only that portion of a sample which could be filtered in less than one-half hour. Care was taken to stir the water during filtration so that the percentage of PbS filtered out would correspond to the percentage of water filtered. The results of these analyses were inconclusive.

It was suggested that lead carrier recovery could be increased by the addition of a drop of ammonium hydroxide to the sample after hydrogen sulfide saturation (20). The procedure and results are shown in Appendix B, page 85. Though the experimentation was limited, an average increase

of 14.5 per cent in recovery of lead carrier was obtained.

The results of all work performed with the hydrogen sulfide precipitation method and its modifications were erratic; but the main reason for rejecting the method is shown in the footnote found in column 3, Table 2. A pink precipitate which rapidly clogged the millipore filter paper was obtained upon filtration of these samples. Attempts to remove the material by filtration of the samples prior to precipitation failed. It was felt that the pink precipitate was due to either free elemental sulfur, colloidal clay, or an unknown sulfur compound that may have been present in the samples. Since the presence of this material made filtration unpredictable, it was decided to develop methods of radon analysis which would not require filtration, but which would retain the advantages of speed, accuracy, and low cost.

In a very brief experiment carried out in the field, 500 ml of water from sampling point No. 39 (see Appendix C, page 88, for location) was filtered directly through a millipore type HA filter. The alpha count obtained was only about 860 cpm versus about 9,000 cpm expected with the dithizone method (Chapter IV) for equal decay times. The efficiency of radon daughter recovery was too low to be useful in the analysis of samples with low radon content. The sample was then re-filtered through a second filter and a count rate of about 237 cpm was obtained, which showed that even the retention of suspended matter was not complete. Consequently, further experimentation was discontinued.

CHAPTER III

DE-EMANATION AND SCINTILLATION DETECTION APPARATUS AND TECHNIQUES FOR RADON AND RADIUM ANALYSIS

The method and equipment developed for the analysis of radon and radium in water are based on the fact that radon is an inert gas. Therefore, water containing radon tends to lose radon rapidly to the air with which it comes in contact. The radon is removed by passing air through the water; and both radon and air are collected in a flask for alpha scintillation counting (19).

The portion of the uranium decay scheme of interest in this analysis, from radium-226 to lead-206, is shown in Fig. 2. When radon is first removed from the water sample, it is free of all daughter products. The radioactive growth equations (22) may then be used to predict the total alpha activity of radon and its daughters at any subsequent time.

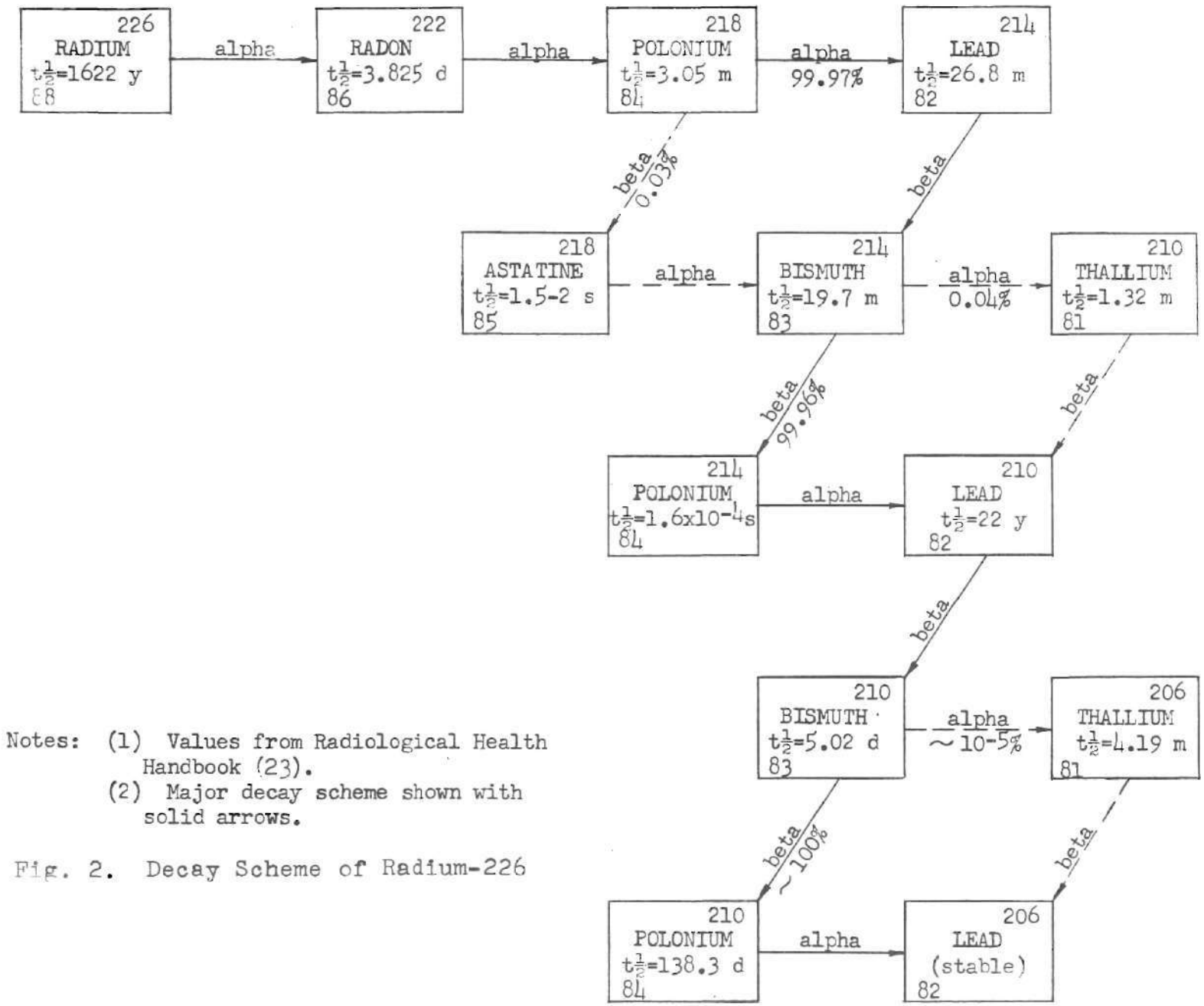
$$\text{Radon activity at any time } t = \frac{N_1\lambda_1}{N_o\lambda_1} = e^{-\lambda_1 t} \qquad (2)$$

where, N_o = number of radon atoms initially present

N_1 = number of radon atoms present at time t

λ_1 = the decay constant of radon (λ = 0.693/half-life)

The activity of the first daughter at any time t relative to the initial radon activity may be expressed as:



Notes: (1) Values from Radiological Health Handbook (23).
(2) Major decay scheme shown with solid arrows.

Fig. 2. Decay Scheme of Radium-226

$$\frac{N_2\lambda_2}{N_o\lambda_1} = \frac{\lambda_2}{\lambda_2-\lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \qquad (3)$$

where, N_2 = number of atoms of the first daughter at time t

λ_2 = decay constant of the first daughter

and using a similar system of notations:

The activity of the second daughter at any time t relative to the initial activity of radon is given by:

$$\frac{N_3\lambda_3}{N_o\lambda_1} = \lambda_2\lambda_3\left[\frac{e^{-\lambda_1 t}}{(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)} + \frac{e^{-\lambda_2 t}}{(\lambda_2-\lambda_1)(\lambda_2-\lambda_3)} + \cdots + \frac{e^{-\lambda_3 t}}{(\lambda_3-\lambda_1)(\lambda_3-\lambda_2)}\right] \qquad (4)$$

The activity of the n^{th} member of such a chain at time t relative to the initial activity of radon, may be expressed as:

$$\frac{N_n\lambda_n}{N_o\lambda_1} = (-1)^{n-1}(\lambda_2\cdots\lambda_n)\left[\frac{e^{-\lambda_1 t}}{(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)(\cdots)(\lambda_1-\lambda_n)} + \cdots + \frac{e^{-\lambda_n t}}{(\lambda_n-\lambda_1)(\lambda_n-\lambda_2)(\cdots)(\lambda_n-\lambda_{n-1})}\right] \qquad (5)$$

In order to facilitate the use of the equations above, two simplifying assumptions may be made. The first is that lead-210 and its daughters will not build up to significant

concentrations during the interval between radon separation and alpha counting. Lead-210 is initially absent and builds up on the basis of a twenty-two year half-life. A second simplifying assumption is the inclusion of only the major path of branching decay. The largest branch neglected is the alpha decay of bismuth-214 to thallium-210 which includes only 0.04 per cent of the total bismuth decay.

At any time after radon isolation, with the assumptions listed above, the radioactive growth equations may be used to predict the ratio of the combined radon-222, polonium-218, and polonium-214 alpha activity to the initial radon activity only. Equations 2, 3, and 5 (n=4) have been evaluated and combined to yield:

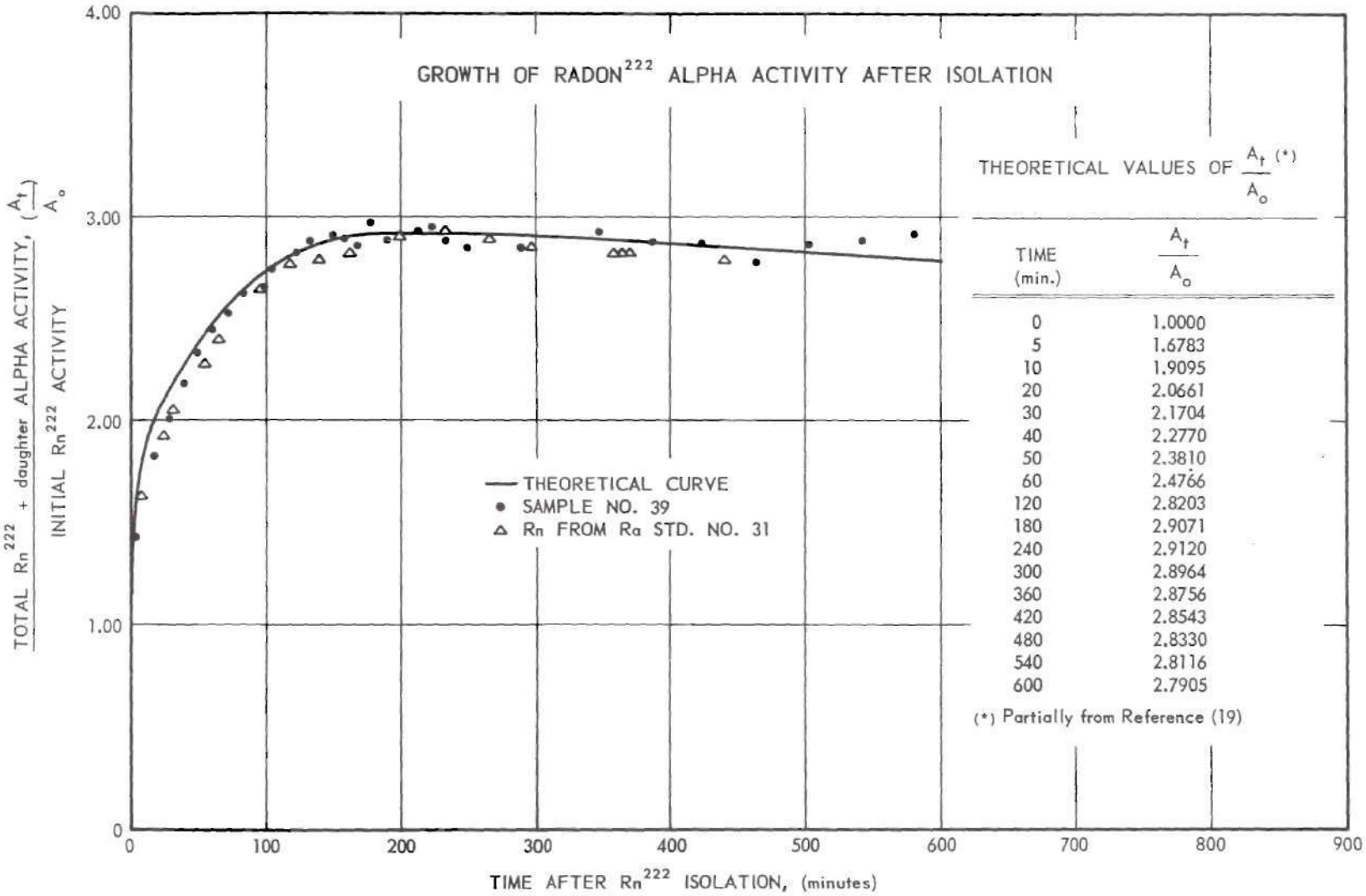
$$\frac{A_t}{A_o} = 3.009\ e^{-0.0001258t} - 1.024\ e^{-0.2273t}$$

$$- 4.280\ e^{-0.02586t} + 3.295\ e^{-0.03519t}$$

where, A_t = activity of Rn^{222} + Po^{218} + Po^{214} at any time t

A_{Rn} = activity of Rn^{222} at t = 0

A plot of the theoretical growth equation above is shown in Fig. 3. This curve represents the rising alpha activity from radon. Superimposed on this curve are experimental points tracing the growth of alpha activity from both a standard solution of radium-226 (radium standard No. 31, Appendix D, page 91) and from water obtained at a



THEORETICAL VALUES OF $\frac{A_t}{A_o}$ (*)

TIME (min.)	$\frac{A_t}{A_o}$
0	1.0000
5	1.6783
10	1.9095
20	2.0661
30	2.1704
40	2.2770
50	2.3810
60	2.4766
120	2.8203
180	2.9071
240	2.9120
300	2.8964
360	2.8756
420	2.8543
480	2.8330
540	2.8116
600	2.7905

(*) Partially from Reference (19)

Fig. 3. Growth of Radon-222 Alpha Activity After Isolation

residence in Raymond, Maine, (sampling point No. 39). These points were determined by means of repeated alpha analyses extending over a period of time after radon separation. The experimental values followed the theoretical growth curve quite closely except for the low values obtained during the initial two-hour period. These initial low values were attributed to the rapid increase in activity during the counting period which produced an error when the average count rate was plotted at the midpoint of the counting interval. A five-minute counting interval was chosen to minimize this error and still maintain a significant total number of counts.

Equipment and Instrumentation

The equipment required for the analytical procedure under consideration was not commercially available. As discussed below, these items included glass sampling devices or bubblers, scintillation flasks, and the scintillation detection unit. Each of these was designed and developed for these studies at the Sanitary Engineering Laboratories at the Georgia Institute of Technology.

As a result of preliminary studies, a special type of glass bubbler was developed for the purpose of separating radon from water. A sketch of this device is shown in Fig. 4. A number of requirements had to be satisfied by this bubbler. These were: (1) the volume had to be large enough to hold a

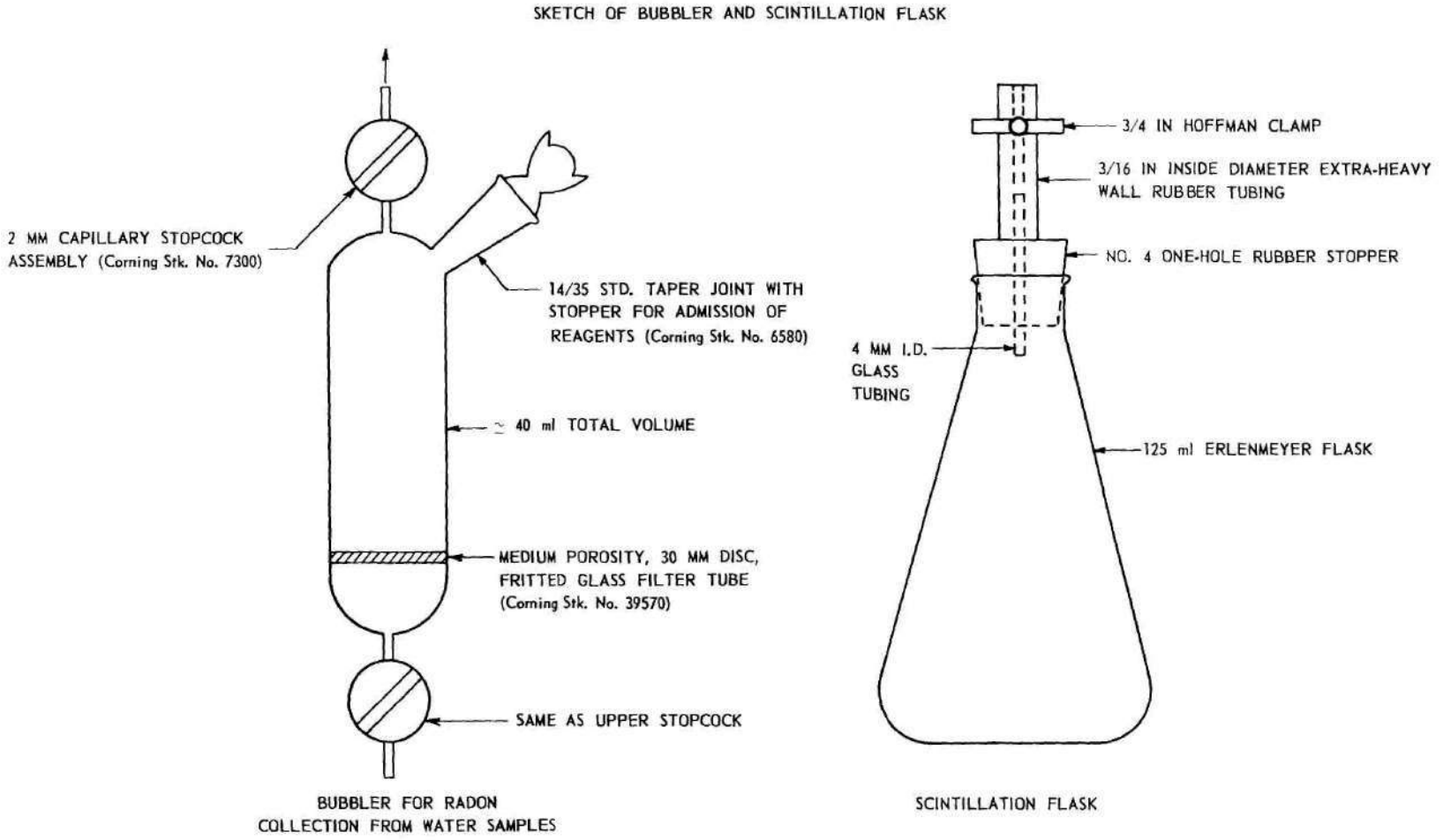


Fig. 4. Sketch of Bubbler and Scintillation Flask

sample containing sufficient radon for analysis, (2) a favorable depth-to-diameter ratio was necessary to insure maximum time of contact between air and water, (3) an air space above the sample was required to allow expansion of the water during bubbling, and (4) a porous plate was required below the sample to disperse the air into uniform bubbles.

Consideration of the requirements listed above led to a choice of approximately 40 ml as the bubbler volume. Twenty-five ml of this volume was provided for the liquid sample and the remainder as a space to provide for the expansion of the liquid upon aeration. To provide the necessary agitation and an adequate air-water interface for the de-emanation of radon, medium porosity fritted glass filters (Fig. 4) were employed as diffuser plates. Stopcock assemblies with 2 mm bore diameter were employed to better control the flow of air through the bubbler assembly. A tapered glass stopper was provided for the admission of reagents and the water sample. Bubblers numbered 1 through 10 were produced from "Pyrex" glass components manufactured by Corning Glass Works, while bubblers numbered 11 through 50 were produced from components obtained from Consolidated Glass Works.

The scintillation flask size was determined by the diameter of a three-inch photomultiplier tube and to provide a volume adequate to insure complete and efficient radon removal from the bubbler. A 125-ml Erlenmeyer flask was

selected to produce a ratio of greater than one-to-five between volume of liquid to volume of de-emanation gas. Holaday, Rushing, et al (19) found a ratio of one-to-four to produce efficient radon removal from water.

The Erlenmeyer flasks (Fig. 4) were equipped with an one-hole rubber stopper fitted with a section of glass tubing, a short piece of rubber pressure tubing, and a hose clamp. The stopper assembly was provided so that the flasks could be evacuated and would hold a vacuum for several hours. A Cenco vacuum pump* was used to evacuate the flasks.

To detect alpha particles from the radon activity in the water samples, silver-activated zinc sulfide phosphor was used as a scintillation screen. The screen was inside the flask, since alpha particles have an extremely short range in glass. To provide the scintillation screen, the inside of the flasks were coated with a layer of zinc sulfide crystals** as outlined by Harris, LeVine and Watnick (24) in a similar procedure. The inside end of the stopper was coated, but the inside bottom of the flask was not. The clear flask bottom provided a window for a clear light path to the photomultiplier tube.

---

*Cenco-Hyvac model produced by the Central Scientific Company, Chicago, Illinois (0.0003 mm Hg vacuum).

**The thickness of the zinc sulfide layer was found, by weighing 19 samples, to be 5.71 mg/cm^2 and to have a 95 per cent confidence interval of $\pm$ 0.85 mg/cm^2.

Three types of zinc sulfide phosphor* were utilized. Zinc sulfide produced by E. I. duPont de Nemours and Company was used for most of the sampling. However, small quantities of both General Electric and U. S. Radium Corporation phosphors were used toward the end of the sampling program. The U. S. Radium Corporation's zinc sulfide had a greater light-holding capacity after exposure to light and was therefore not economical in counting time. At least five minutes were required for the retained light to die out completely, whereas, with the duPont phosphor, only about fifteen seconds were required. Harris, LeVine and Watnick (24) report that "The zinc sulfide required at least one and one-half hours in total darkness before the effect of exposure to light was minimized."

The scintillation technique is based on the phenomenon that when radiation is absorbed by certain materials, photons of light are emitted. For example, when alpha particles bombard a crystal of silver-activated zinc sulfide, scintillations or pulses of light are emitted from the zinc sulfide phosphor. These scintillations of light can be amplified and counted as pulses of electricity. The transducer which

---

*1. E. I. duPont de Nemours and Co., Luminescent Chemical, Type D, Lot 68.

2. General Electric Company, TV Phosphor.

3. U. S. Radium Corporation, Radelin Phosphor, Color Number 920B.

is used in this application is the photomultiplier tube. The photomultiplier tube has an activated cathode which emits electrons each time photons of light strike it. These electrons are cascaded back and forth inside the tube, producing secondary electrons, until enough electrons are available at the anode to produce a current pulse. This current pulse is converted to a voltage pulse which is amplified many times to produce sufficient voltage to trigger the scaler unit.

A special field scintillation type detection unit, not commercially available, was designed and assembled at the Georgia Institute of Technology and is shown diagrammatically in Fig. 5. The detection unit consisted of four principal parts: (1) a photomultiplier tube, (2) a preamplifier, (3) a pulse amplitude discriminator, and (4) a low-voltage power supply. A schematic diagram of the complete radon detection unit is shown in Fig. 6.

A Dumont Model 6363, ten-stage, three-inch photomultiplier tube was used. The high voltage necessary for operation of this tube was supplied by a Nuclear-Chicago, Model 186 scaler unit.

To increase the output signal voltage of the photomultiplier to a more usable level and to lower the output impedance of the photomultiplier tube to a level suitable for driving a length of coaxial cable, a preamplifier was installed in juxtaposition to the photomultiplier tube. The

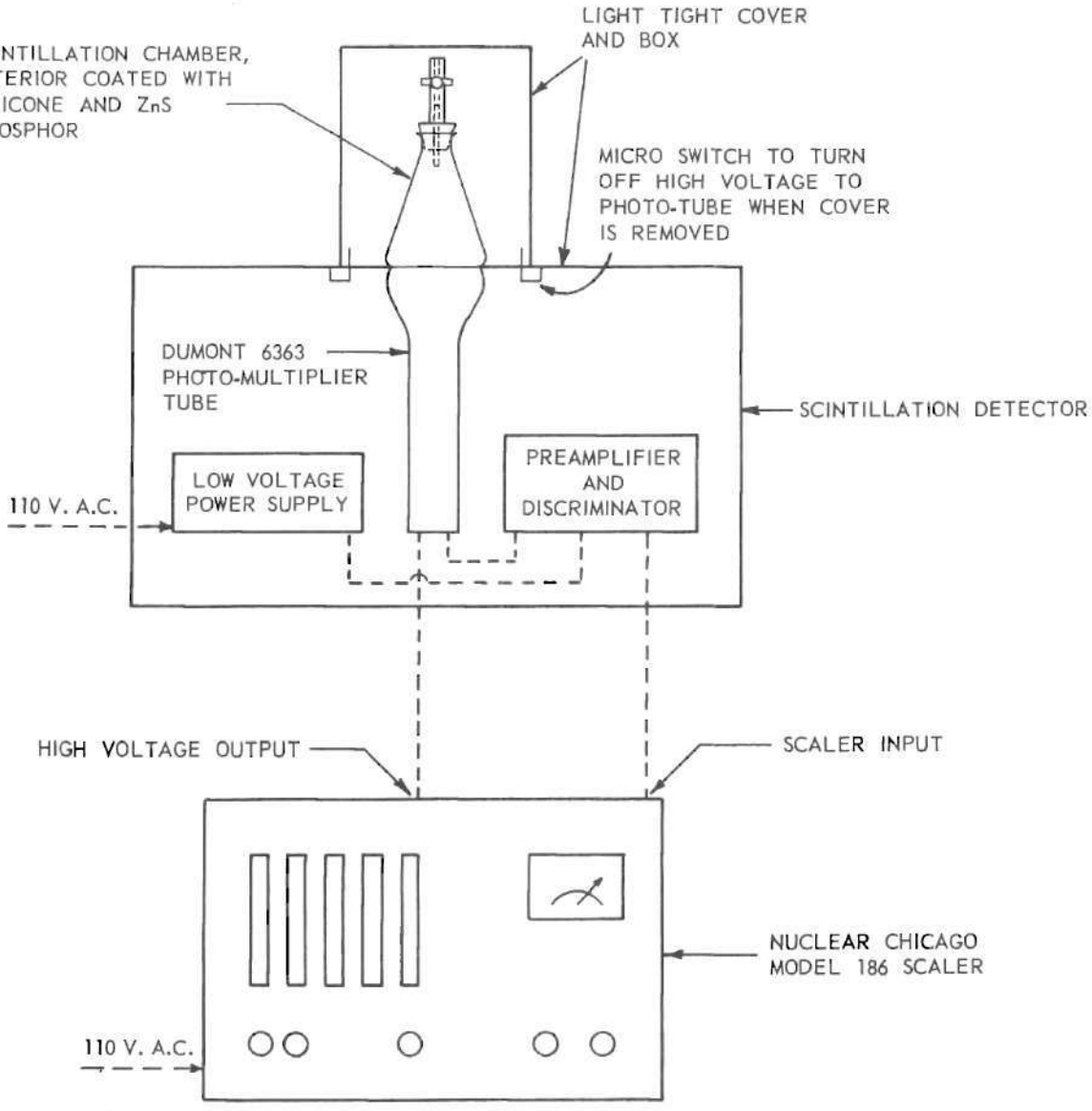


Fig. 5. SKETCH OF SCINTILLATION DETECTOR AND SCALER

SCHEMATIC DIAGRAM OF SCINTILLATION DETECTOR AND SCALER

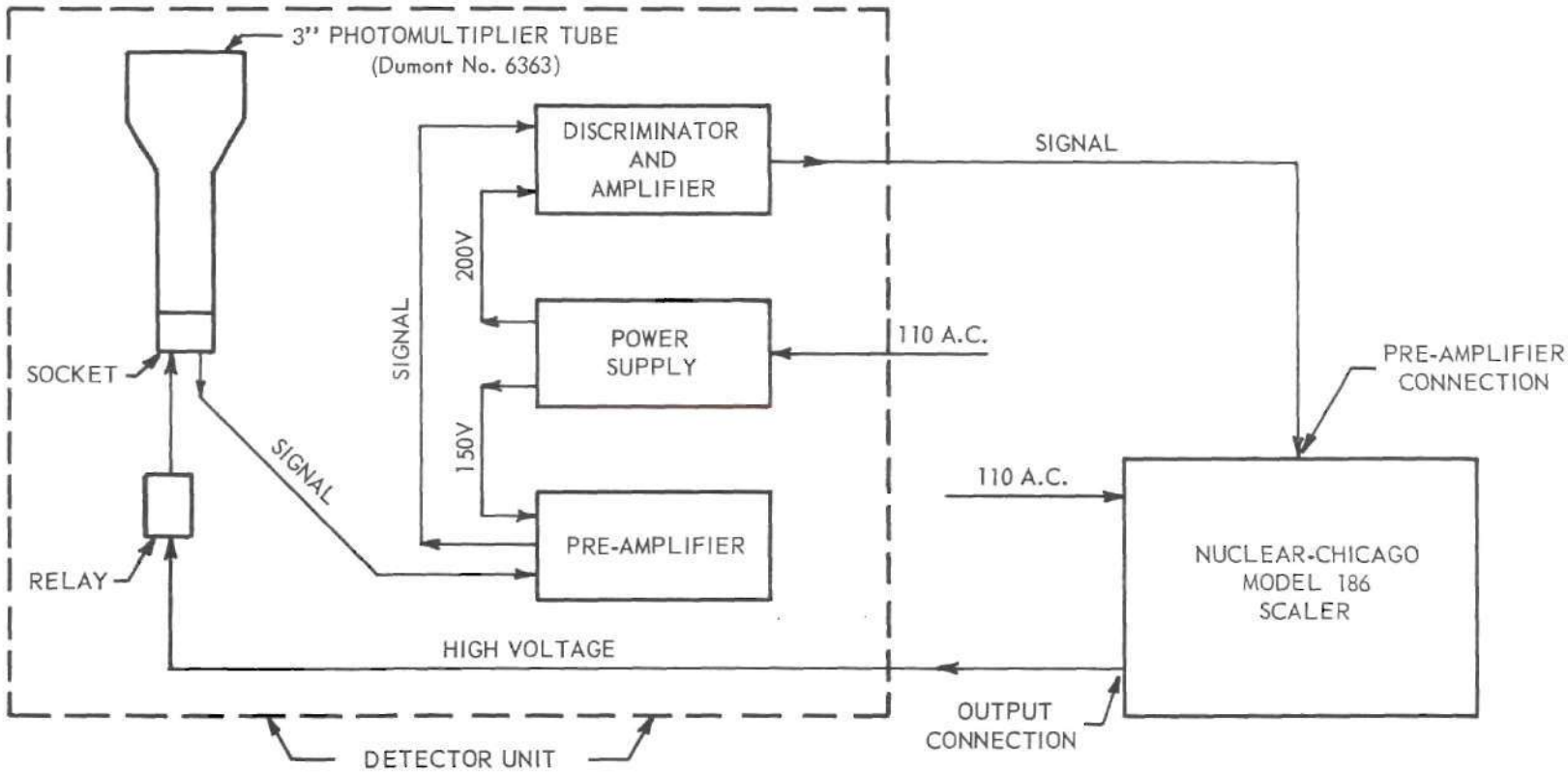


Fig. 6. Schematic Diagram of Scintillation Detector and Scaler

schematic diagram for this preamplifier is shown in Fig. 14, Appendix E, page 94.

The amplifier-discriminator performed two tasks. The first was to further amplify the signal from the preamplifier before the signal was introduced to the discriminator section. The other task was to pass signals above a preset level and to reject those below that level. This allowed the random noise pulses which are usually much below the average signal level to be removed from the input signal, which includes all the noise. The schematic diagram for this unit is shown in Fig. 15, Appendix E, page 95.

The low-voltage power supply was required because the scaler power supply was inadequate to power all the components of the detection system. This unit was voltage-regulated to make possible reproducible readings. As an additional safeguard, a 250-Watt Sola transformer regulator was used in the AC line to the power supply. This combination produced a most stable regulation under all conditions encountered in Maine and New Hampshire. A schematic diagram of this unit is shown in Fig. 16, Appendix E, page 96.

Procedure for Performing Radon Analysis

The sampling and analytical procedures have evolved, after a summer in the field, into a system emphasizing speed while preserving accuracy. The analysis involves the collection of a water sample with minimum aeration, removal and

collection of the radon from the water, and analysis by scintillation counting.

Bubbler and Scintillation Flask Preparation.--Bubblers were prepared for use by thorough rinsing with distilled water to remove soluble impurities. To prevent progressive clogging of the fritted glass, the upper section of the bubbler was first rinsed with distilled water. A small quantity of water was then forced into the lower section through the capillary tube, the bubbler inverted and a vacuum applied to the upper stopcock in order to pull the water through the fritted glass in the direction of normal air flow. This was found to be the most expedient way to remove any suspended matter retained by the upper surface of the fritted glass.

After cleaning, the bubbler was prepared for sampling by adding one ml of concentrated nitric acid through the tapered joint to produce an approximate 0.5 N acid concentration in the sample. The high pH of the resulting solution tended to keep dissolved materials in solution and reduced contamination of the bubbler. The final preparatory step before sample collection was to weigh the bubbler for subsequent determination of sample volume.

As shown in Fig. 4, the scintillation chamber was a 125-ml Erlenmeyer flask coated with ZnS. The first step in the preparation of a zinc sulfide screen was to swab the sides of the flask with a solution of approximately one part silicone grease to ten parts chloroform by volume. The

chloroform evaporated rapidly and left a layer of grease to hold a uniform coating of zinc sulfide powder. The walls were coated from the base of the neck to the edge of the flat bottom.

Care was taken to prevent contact of the zinc sulfide powder with the bottom of the flask, as a small amount would cling to the glass, upsetting the geometry and interfering with the passage of light. Coating was performed by tilting the flask and pouring zinc sulfide from a test tube down the wall. By careful tilting and rotation of the flask a uniform coating was obtained without contact of the zinc sulfide with the bottom of the flask. Excess zinc sulfide was removed by inverting the flask and tapping the neck. In order to obtain a slight increase in geometry, the bottom faces of the rubber stoppers were also coated.

The scintillation flasks were found to become contaminated by radon daughters after each radon sample with a concentration above 500 $\mu\mu$c/l and therefore had to be washed and recoated. To conserve flasks and to maintain fresh zinc sulfide coating, each flask was first used for a background count, then for a sample, and finally recoated. The silicone grease layer prevented contamination of most of the surface of the flask, and no permanent increase in flask activity was noted. The best procedure for washing the flasks was scrubbing with a mixture of chloroform and detergent, then washing with the detergent alone, and finally rinsing with

distilled water.

Sample Collection.--Samples were collected directly from faucets to measure as nearly as possible the true radon concentration exposure of the consumer. Before collecting a sample, the faucet was turned on for a period of at least one minute to insure that the sample came from the pressure tank or the well. Since radon tends to escape quite readily, any turbulence in the flow from the faucet would result in a partial loss of radon. To minimize this error, aerators and spray nozzles were removed, and a uniform and smooth flow of water was obtained from the faucet. The bubbler was filled directly under the stream, quickly removed, and stoppered. The maximum time for the entire operation was not allowed to exceed three or four seconds.

Radon De-emanation.--Radon was removed from the bubbler and collected in the scintillation flask. The upper capillary tube of the bubbler was connected with the scintillation flask. The rubber tube clamp and one stopcock of the bubbler were opened, and the second stopcock was used to regulate the "vacuum-produced" flow of air.

The air flowing through the bubbler was dispersed by the porous glass plate into small bubbles which scrubbed the radon from the sample. Care was necessary, when the flow of air was started, that the vacuum was not applied too rapidly or some of the liquid sample would be drawn into the the scintillation flask, damaging the ZnS coating and

resulting in the inclusion of extraneous radioactive materials in the subsequent analysis. After bubbling had ceased, the clamp on the rubber tubing was tightened to seal off the radon in the flask, and the bubbler was stored for transportation to the laboratory. Bubbling was performed as rapidly as possible within the limit imposed by the space provided in the bubbler for sample expansion.

After bubbling had ceased during separation, a partial vacuum remained in the scintillation flask because of head loss in the flow of air through the bubbler. This loss is proportional to the porosity of the fritted glass plate and to the depth of the water sample in the bubbler. Consequently the remaining vacuum varied with different sample depths and bubbler porosities. Since the range of alpha particles in air is a function of the air density, the proportion of alpha particles reaching the ZnS in the scintillation flask would vary with the partial vacuum. To maintain a more constant counting efficiency, the pressure in the flask was equalized to atmospheric pressure. The air was introduced gently to prevent radon loss from turbulence. The flask was then sealed as rapidly as possible after an equilibrium pressure had been reached.

Air was used to remove the radon from the water. Therefore, special measures were necessary to correct for the radon concentration of the air. The problem was overcome by taking an air sample at each radon sampling point,

using only a scintillation flask. The "air sample" flask was counted in the laboratory and used in the same manner as a background count for calculations. It was assumed that by de-emanating in the laboratory, a single background sample of laboratory air would serve a large number of samples bubbled during a short period. Experience, however, showed that radon was often lost by stopcocks opening during transportation to the laboratory.

Laboratory Analysis for Radon.--The analysis of samples in the laboratory proved to be a rapid and simple procedure. The bubblers were re-weighed to determine the precise sample volume; and the sample and background flasks were counted to complete the analysis.

Special care was found to be necessary in two steps of the laboratory analysis. First, the flask should be centered on the photomultiplier tube to insure constant geometry. Second, it was necessary that the sample be separated at least four hours before counting was started. This time interval insured that the radon and daughters were in equilibrium (Fig. 3) and were changing only slowly with the radon half-life. Under these conditions, no correction for decay during counting was necessary, over normal counting periods, because of the slow rate of change in the total activity.

In the work presented, a preset counting time of twenty minutes was used for all radon analyses, with back-

ground counts of five-minute duration. A Nuclear-Chicago scaler, Model 186, was used at an operating voltage of 1,400 volts. However, preamplification and discrimination units were acting together in both the scaler and the detector, but were not calibrated. Therefore, the operating levels were unknown. Typical field and laboratory data sheets are shown in Appendix F, page 91, along with sample calculations of the activity of a sample.

Calibrations of Method and Equipment

A primary standard solution of radium, which contained 2.000 ± 0.014 μc of radium-226 in 5 ml of five per cent by weight of HNO_3, was obtained from the National Bureau of Standards, Washington, D. C. Secondary standards for field use were prepared by successive dilutions from the primary standard to obtain concentrations of 2, 20, 200, and 2,000 $\mu\mu$c/ml. Portions of these secondary standards were sealed into 5 cc ampoules for later use. To insure a high degree of accuracy for secondary standards, the ampoules were weighed before and after filling as a check on the volume of solution contained in each ampoule.

The computations and activities for the secondary standards used in the field work are shown in Appendix D, page 97. In order to transport the radium solutions safely, a container was constructed consisting of a pair of 2" x 4" x 36" pieces of board nailed together with drilled holes for

individual ampoules. The ampoules were packed in cotton and the top and bottom, consisting of 1" x 4" x 36" pieces of board, were secured in place with bolts and wing nuts.

The determination of the counting efficiency involved the transfer of a known volume of a secondary standard to a bubbler, the addition of distilled water to bring the volume to 25-30 ml, a period of aging to allow radon build-up, radon removal as for a sample, and counting the scintillation flask.

Before storing the standard solution in the bubbler for radon build-up, it was important that all radon present be removed. A definite reference time would then be established for radon build-up calculations. This was accomplished by drawing air, for several minutes, through the standard solution by means of a vacuum applied to the top of the bubbler. A partial vacuum was left in the bubbler to insure that any leakage during storage would be inward and would not result in radon loss. The period of aging depended on the desired per cent of radon equilibrium and on the time available. Radon build-up is a function of the half-life as shown by the following equation:

$$\frac{N_1\lambda_1}{N_o\lambda_o} = 1-e^{-\lambda_1 t} \qquad (6)$$

where, $N_o\lambda_o$ = activity (constant activity of radium)

$N_1\lambda_1$ = activity of radon at time t

λ_1 = decay constant of radon

t = time after isolation of radium

Eight days was the minimum storage time used, to allow the radon activity to reach approximately 80 per cent of the radium activity, though longer times tended to minimize any error due to incomplete initial radon removal.

The analyses for the counting efficiency determinations were performed by de-emanating the radon, from a radium standard contained in a bubbler, into a scintillation flask and counting. A comparison of the theoretical activity with the observed activity yielded the over-all efficiency of the analysis. This method of calibration had the advantage that the bubblers containing the standard solutions could be re-used as often as desired. After each purging operation, as previously described, the bubbler could be stored for radon build-up until the next analysis. Thus, a series of checks on the efficiency was made over a period of time employing the same standard solutions.

The results of the repeated analysis of a group of standards are shown in Table 3. Since efficiency varied with time, a graph of efficiency versus time was employed in calculations. This graph is illustrated in Fig. 7. Points plotted are the averages of standards analyzed on a particular day. The efficiency of scintillation detection varied during the period of use from about 80 per cent to 54 per cent. This variation may be explained in part by the different ZnS phosphors used and in part by the decay in sensitivity of the photomultiplier tube.

Table 3

Counting Efficiency Determination

Standard No.	Date of Analysis	Calculated Counting Efficiency (%)
1	7/27/59	68.5
2	7/27/59	73.4
31	7/27/59	73.9
32	7/27/59	68.5
1	8/7/59	61.4
2	8/7/59	61.4
31	8/7/59	66.1
32	8/7/59	61.3
1	8/17/59	52.5
2	8/17/59	54.9
31	8/17/59	56.7
32	8/17/59	60.8
1	8/30/59	70.7
2	8/30/59	74.5
23	8/30/59	62.5
31	8/30/59	65.6
32	8/30/59	68.6
1	9/18/59	61.7
2	9/18/59	63.2
23	9/18/59	67.4
31	9/18/59	59.7
32	9/18/59	64.5

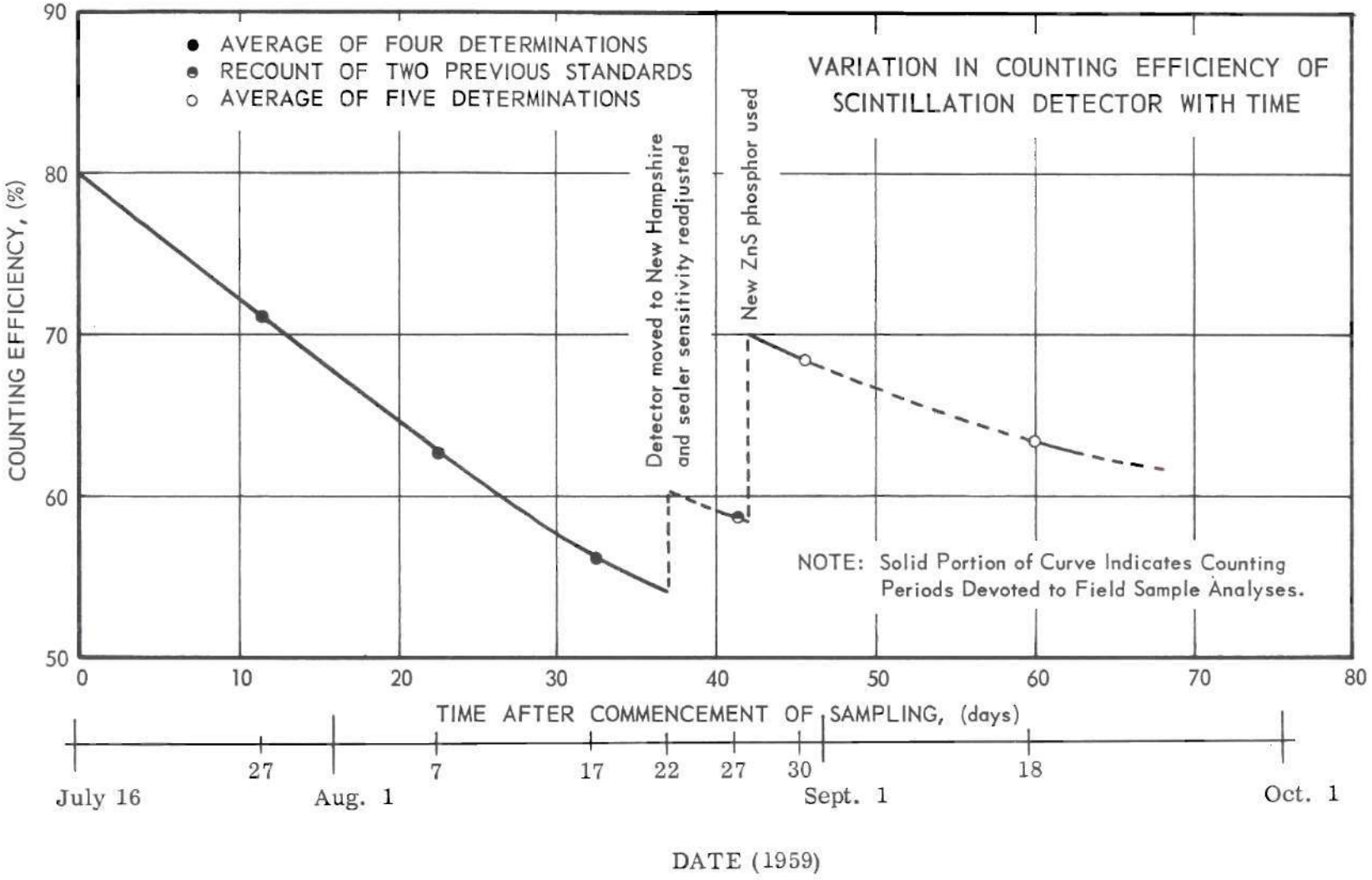


Fig. 7. Variation in Counting Efficiency of Scintillation Detector with Time

After the initial phase in Maine was completed, the laboratory was moved on August 22, 1959, to New Hampshire, where the scaler sensitivity had to be re-adjusted after mechanical repairs were performed. Standards number 31 and 32, originally analyzed on August 17, 1959, and preserved, were re-counted to establish the new efficiency, resulting in the portion of the curve (Fig. 7) between August 22 and August 27. A new supply of ZnS (General Electric Company), which was more sensitive to light than that used previously, was obtained on August 27. This resulted in an increase in efficiency as shown in Fig. 7. Some doubt exists about the shape of the curve from August 27 to September 14, since a third brand of zinc sulfide (U. S. Radium Corp.) was substituted before the fifth standarization series was run, resulting in only one set of standards being run with each brand of phosphor. However, since the slope of the decay curve through the two points is comparable to the shape of the initial part of the curve, the same trend was continued. Errors in the results obtained during the latter period were minimized by the fact that counting was done only during periods slightly before and after each of the two efficiency determinations.

Differences between bubblers existed due to the use of diffuser plates from two manufacturers. To compare data obtained with different bubblers, and to evaluate any differences in results, it was necessary to separate the radon

removal efficiency from the over-all efficiency of the process. For each of the two types of bubblers, separate radon removal efficiencies were established for a representative group by successive bubbling of a sample until all measurable radon was removed. It was found that two or three bubblings were sufficient to remove all radon above background counting levels. The sum of the activities obtained represented the total radon concentration of each sample. The radon removal efficiency was determined by dividing the activity from the first de-emanation by the total activity measured. The resulting values were applied to each sample calculation to compensate for incomplete removal of radon from the water.

The radon removal efficiency was determined for several standards as a part of the counting efficiency determination, resulting in the values shown in Table 4. The individual removal efficiencies were applied to the corresponding counting efficiency determinations and the average of all removal from the remaining standards. Since de-emanation is a physical process, the average removal of 99.3 per cent was assumed to be valid for sample in bubblers 1 through 10 and was applied to all subsequent analyses with these bubblers. To obtain an estimate of the removal efficiency of radon from bubblers 11 through 50, four bubblers were chosen at random, removal efficiencies were determined, and the average removal was taken as a correction factor in all

Table 4

Radon Removal Efficiency From Standard Solutions

Std. No.	Bubbler No.	Date	No. times Bubbled	Removal in 1st Bubbling (%)
31	5	7/27/59	2	98.9
32	6	7/27/59	2	99.2
31	5	8/7/59	2	99.3
32	6	8/7/59	2	98.1
31	5	8/17/59	2	99.6
32	6	8/17/59	2	99.1
23	9	8/30/59	2	99.8
31	5	8/30/59	2	99.5
32	6	8/30/59	2	99.8
1	3	9/18/59	2	~100
2	4	9/18/59	2	97.3
23	9	9/18/59	2	99.5
31	5	9/18/59	2	99.6
32	6	9/18/59	2	98.8
				Average = 99.3%

Table 5

Radon Removal Efficiency From Water Samples*

Bubbler Number	Date	No. Times Bubbled	Removal by 1st Bubbling (%)	Removal of Remainder by 2nd Bubbling
23	8/21/59	3	90.4	91.1
36	8/21/59	3	84.2	89.2
41	8/21/59	3	91.9	93.1
44	8/21/59	3	88.1	88.9
			Average of 8 =	89.6%

*Sampling Point No. 39.

sample analyses employing these bubblers. The results are shown in Table 5. The average removal efficiency was found to be 89.6 per cent.

Although a large discrepancy exists between the removal efficiencies found for bubblers 1 through 10 and 11 through 50, the difference may be partially justified. Radon removal is a function of bubbler size and contact time; and bubblers 11 through 50 were inferior to bubblers 1 through 10 in the quality of the fritted glass disc. The fritted discs in bubblers 11 through 50 produced very large bubbles from only a small portion of the glass disc. The larger bubbles of bubblers 11 through 50 resulted in reduced contact surface and time, and therefore, produced less efficient radon removal.

Interferences

Radon is the only gaseous product in the natural uranium decay series. Since the method involves only the removal of gases, there is no possibility of interference from other radioactive materials from this series. Radon present in the atmosphere is a serious interference in the analysis for radium, but is accounted for in radon analysis if an air sample is used in background determination. The radium count rates encountered were very low; therefore, the addition of atmospheric radon during bubbling caused background count rates to be several times higher than net sample

count rates. The typical background counting rate was about five cpm although 100 cpm was exceeded in several instances. The alpha activity of air at typical sampling points is shown in Appendix G, page 102.

A second possible source of interference is the alpha emissions from thoron (Rn-220) or actinon (Rn-219) gas in the water sample, if thorium or actinium are present. Thoron has a half-life of 54.5 seconds, while actinon has a half-life of 3.92 seconds. Because of their extremely short half-lives, neither substance is likely to persist in measurable quantities long enough to move from a well, through the pressure tank, and through the household distribution system except in concentrations approaching equilibrium with radium. Once removed from the bubbler into the scintillation flask, however, interference would result which would be proportional not to the thoron or actinon activity introduced, but to the number of atoms introduced. In the case of an isolated parent which disappears in a few minutes, the activity at some later time will be composed of some mixture of daughters, each decaying with its own half-life, and the total number of atoms present would be equal to the number of atoms of the parent originally present. Consider, for example, equal amounts, in $\mu\mu$c/l, of two radioactive substances at a given time:

$$\text{Activity} = \frac{0.693N}{t_{\frac{1}{2}}}$$

where, N = number of atoms

$t_{\frac{1}{2}}$ = half-life

Equating the activities of the two materials:

$$\frac{0.693\ N_1}{(t_{\frac{1}{2}})_1} = \frac{0.693\ N_2}{(t_{\frac{1}{2}})_2}$$

$$\frac{N_1}{N_2} = \frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2}$$

Thus, the ratio of the number of atoms of two substances of equal activity is equal to the ratio of their half-lives. Therefore, for equal number of atoms the ratio of activities will be given by the expression:

$$\frac{A_2}{A_1} = \frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2} \qquad (7)$$

Most of the atoms present as daughters of thoron will be in the form Pb-212 at the time of counting, since it is the first relatively long-lived daughter product. Lead-212 has a half-life of 10.6 hours, therefore, the following approximate reduction in activity from thoron is obtained:

$$\frac{A_2}{A_1} = \frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2}$$

let, A_1 = thoron activity

A_2 = lead-212 activity

$$\frac{A_2}{A_1} = \frac{54.5 \text{ sec.}}{38{,}160 \text{ sec.}} = 1.428 \times 10^{-3}$$

For actinon, the appropriate daughter is lead-211 with a half-life of 36.1 minutes. The activity reduction factor is given by:

$$\frac{A_2}{A_1} = \frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2} = \frac{3.92 \text{ sec.}}{2166 \text{ sec.}} = 1.810 \times 10^{-3}$$

When it is considered that the proportion of thoron or actinon introduced into the scintillation flask is small because of decay before reaching the collection point, then that this fraction is reduced to 0.14 per cent or 0.18 per cent of the original concentration, it may be seen that interference is negligible. Further reduction in interference is obtained through the production of both alpha and beta daughters from the thoron and actinon atoms introduced; while only alpha daughters are counted. Another reduction in interfering activity is the decay of the thoron or actinon daughters into stable lead during the four-hour period between separation and counting. This is of primary importance in the actinium series where all actinon daughters have short half-lives and the activity is reduced by a factor of about 32 (approximately five half-lives).

Reproducibility of the Method

The reproducibility of the method was determined from the statistical analyses of three different groups of data. The first group of data was composed of the counting efficiencies from several analyses each of five standard solutions. The second group of data consists of nine triplicates of samples from two sampling points. The triplicate samples, besides showing the reproducibility of the over-all analysis, indicate any effect on reproducibility due to the method of sample collection. The third group of data shows the results from eleven different samples of water from sampling point No. 39 (see Appendix C, page 88, for location), collected over a period of about three weeks. This group of samples indicates the effect on the confidence limits of well activity variation with time. The statistical analyses of all three groups of data are shown in Appendix H, page 104.

The statistical test of the results from the standard solutions was based on data from the twenty-two analyses for counting efficiency (Table 3, page 40). These results represent five analyses each of two radium standards with an activity of approximately 400 $\mu\mu$c/l, five analyses each of two standards with an activity of approximately 16,000 $\mu\mu$c/l, and two analyses of one standard with an activity of approximately 40,000 $\mu\mu$c/l. The distribution of data was

tested for normality and the 95 per cent confidence limits were established (25).

Since the arithmetic means of each group of analyses of the standards varied with time (see Fig. 3), the standard deviation could be expressed only on a percentage basis, assuming each group mean to have a value of 100. All the standards were first analyzed as a group. The standard deviation was found to be 5.18 per cent, and it was further calculated that 95 per cent of the time (1.96σ) the values were expected to fall within $\pm$ 10.2 per cent of the mean. The high and low activity standards were also analyzed separately to determine whether the counting error of the low activity standards (approximately six per cent) caused an increase in the confidence interval at the 95 per cent level of significance. The results show a standard deviation of 4.53 per cent and a 95 per cent confidence interval of $\pm$ 8.88 per cent for the high standards. The standard deviation for the low standards was found to be 5.12 per cent with a range of $\pm$ 10.0 per cent (at the 95 per cent level). Therefore, the high activity standards show only a slightly greater reproducibility than those with lower activity.

To analyze the triplicate samples the same statistical methods were used. Since the mean for each group differed, deviations of each sample were again expressed in per cent. The distribution was found quite normal as shown by a value

for the ratio of σ/A.D. of 1.24. The standard deviation is 4.69 per cent and the 95 confidence interval is $\pm$ 9.19 per cent.

From a comparison between the standard deviations of the results from standard solutions and triplicate samples, it can be seen that the method of sample collection exerts no significant effect on the reproducibility of the analysis. Since these statistical analyses could not have been based on absolute values, the accuracy may have been affected, since a constant per cent of radon may have been lost during collection.

Eleven samples taken from sampling point No. 39 during the period from July 29, 1959, to August 21, 1959, were analyzed as a measure of the variation in well activity with time. The deviations were greater, with a standard deviation of 8.53 per cent, and the range of expected values is $\pm$ 16.7 per cent (at the 95 per cent level of significance). The greater value of this standard deviation as compared to that for the standard solutions and replicate samples may be used to measure the variance of the major uncontrollable factor in the analysis, which is the variation of radon activity in the well water with time. The variance of samples from sampling point No. 39 is 72.76, while that of the triplicate samples above is only 22.00. The difference may be considered to be the approximate variance of the activity of the well at sampling point No. 39. This value is 50.76,

which produces a standard deviation of 7.12 per cent and a range of ± 14.0 per cent at 95 per cent confidence. Thus, the confidence interval of the variation in activity with time exceeds that of the reproducibility of the method by a factor of 150 per cent. Smith (2) found the activity of a well in South Paris, Maine, to vary with time during continuous pumping, reaching a maximum about one-half hour after the start of pumping and declining slowly thereafter.

On the basis of the results obtained from the separate analyses of both high and low activity standards, it appears that the method is reproducible to ± 10 per cent at the 95 per cent level of significance over the range of radon concentrations encountered. However, the difference between separate analyses of the same water at different times may be expected to be increased due to the variation in the radon content in the water.

Adaptation of the De-emanation Method to Radium Analysis

The method of analysis described for radon was adapted to radium by a few simple changes in procedure. However, because of the low concentrations of radium normally present in the natural waters and the small sample capacity of the described bubblers, the accuracy of the determination was not adequate unless relatively high radium concentrations were encountered.

The procedure for radium analysis involved storing

a sample of water for a known length of time to allow the build-up of radon from radium, followed by a determination of the radon content. After weighing, the same sample and bubbler used in the radon analysis were used for the determination of radium.

The analytical procedure was as follows: First, and of primary importance, the sample was thoroughly purged of any radon remaining from previous incomplete removal. Only a small fraction of the original radon content remaining in solution would have caused a significant positive error in the analysis. Purging was accomplished by bubbling the sample vigorously for two to three minutes, as described previously for standards. This method eliminated the necessity of transferring the sample, and since care was taken to prevent loss of water during bubbling, the same sample volume used for radon calculations was used for the radium analysis. A partial vacuum was left in the bubbler after complete radon removal to prevent radon leakage by maintaining a negative pressure during storage.

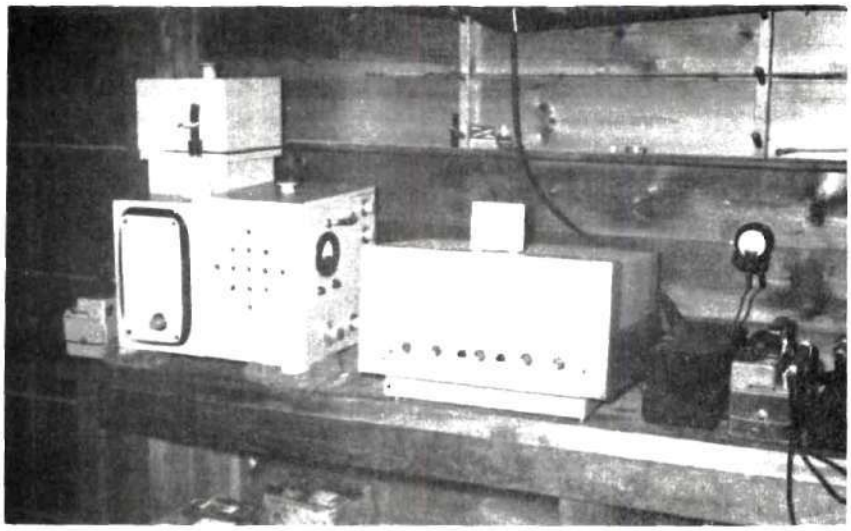
The second step in the procedure was to store the sample for a definite period of time to allow the radon to build up to a known percentage of its equilibrium value with radium. Radium has a half-life of 1622 years (23), and equation 6, page 38, was used to calculate the theoretical radon concentration as a percentage of its equilibrium value with radium after any time. Eight to

ten days of storage was found to be sufficient for a measurable radon concentration. After eight days, the resulting radon activity was about 80 per cent of that of the radium present and was in the range of slowly increasing radon activity. Continuing radon build-up storage beyond the initial period of eight to ten days would tend to minimize errors due to minute quantities of radon left in solution after purging.

After storage was completed, the analysis was performed as for radon except longer counting periods were used and the correction for incomplete equilibrium between radon and radium was applied. The storage time was taken as the period between initial purging of radon and the time the sample was bubbled with a scintillation flask for analysis.

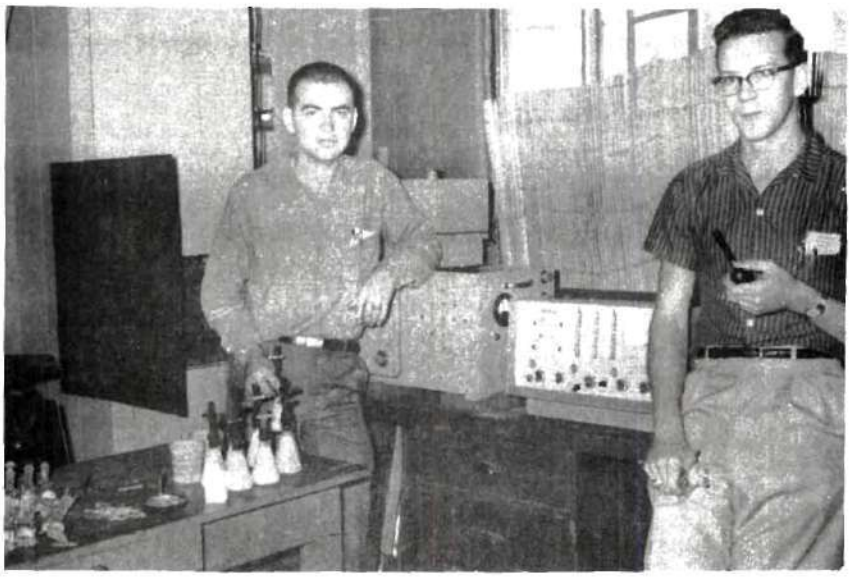
Field Laboratories and Special Investigations

Pictures of Field Laboratories.--A brief description of the field laboratories and equipment used during the summer of 1959 can be obtained from a series of four photographs of the field laboratories in Maine and New Hampshire. Fig. 8 shows a part of the laboratory at Raymond, Maine, where most analyses of samples in Maine were performed. The scintillation detector on the left and scaler on the right take up most of the bench space. The Sola voltage regulator transformer and voltmeter are shown to the right of the



FIELD LABORATORY SET-UP AT RAYMOND, MAINE
(Scintillation Detector and Scaler on Bench)

Fig. 8.



FIELD TEAM IN THE NOTTINGHAM, NEW HAMPSHIRE, LABORATORY

Fig. 9.

scaler.

Fig. 9 shows Mr. Smith and the author, the field survey team, in a corner of the Nottingham, New Hampshire laboratory. In addition to the detector and scaler, a few ZnS coated scintillation flasks and several bubblers are shown on the left hand table ready for radon analysis.

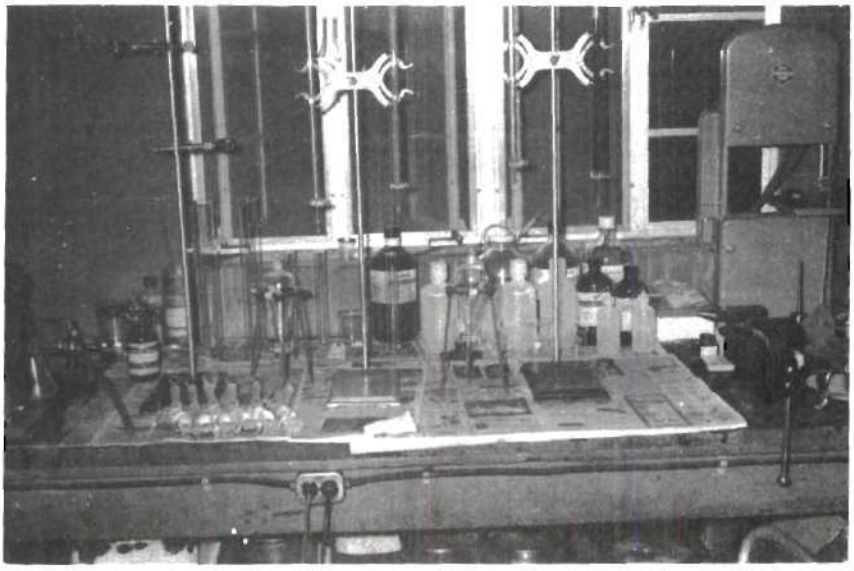
Two photographs of the interior of the New Hampshire field laboratory are reproduced as Fig. 10 and 11. Fig. 10 shows a part of the associated equipment, chemicals and glassware necessary for the performance of these investigations. Much of the laboratory work on the diphenylthiocarbazone method (Chapter IV) for lead-210 analysis in New Hampshire was performed on the laboratory bench shown in Fig. 11.

Identification of the Radon Activity.--Two representative sampling points (No. 22 and 39) were selected in the Raymond, Maine, area for a careful determination of the exact type of radioactivity encountered. Two replicates from each sampling point, or four samples, were counted at several successive times for a precise determination of the rate of decay.

A twenty-minute length of count was used for each measurement. The net counting rate, corrected for background and counting efficiency based on a N. B. S. radium-226 standard, was plotted on semi-log paper. To trace the radon decay, beginning from the time of de-emanation of

ARRAY OF ASSOCIATED EQUIPMENT, CHEMICALS AND GLASSWARE
(Laboratory Set-Up at Nottingham, New Hampshire)

Fig. 10.



SET-UP FOR DITHIZONE ANALYSIS, NOTTINGHAM, NEW HAMPSHIRE

Fig. 11.

one of these samples, the scintillation flask was counted for five-minute intervals over the first seven hours. With decreasing frequency, counting continued for eight additional days. A plot of the observed initial decay for sample No. 39 was presented along with the theoretical and radium-radon standard curves in Fig. 3, page 22.

From a least squares treatment of the data collected after an initial five-hour decay time, a decay curve of best fit by linear correlation was established. This curve is reproduced as Fig. 12. The data exhibited a high degree of reproducibility as shown by a value of 0.995 for the coefficient of correlation. The equation fitted by the method of least squares:

$$A = A_o \, e^{-0.1796t - 0.010} \qquad (8)$$

A = activity of radon-222 at time t

A_o = initial activity of radon-222

t = elapsed time, days

From equation 8, the fifty per cent value, or the half-life, was calculated as 3.80 days. The experimental value compares quite favorably with the established 3.825 days half-life for radon-222 (23). The close agreement between values proves rather conclusively that the gaseous radioelement analyzed is that from the natural uranium series.

The theoretical decay equation for radon-222 is:

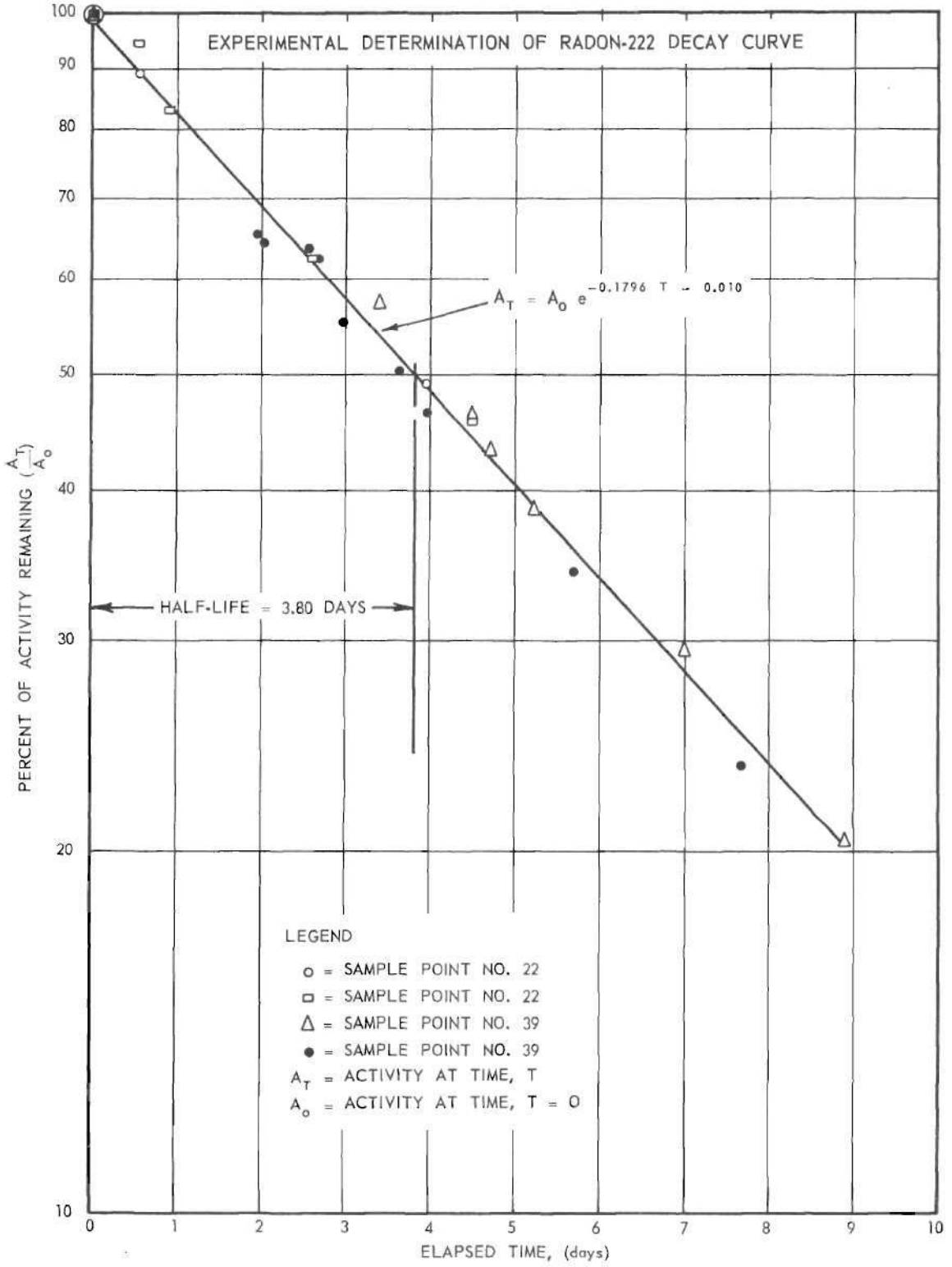


Fig. 12. Experimental Determination of Radon-222 Decay Curve

$$A = A_o \, e^{-0.1812t} \qquad (9)$$

Comparison of Results with Those Obtained by the State of Maine.--The value for radon plus daughters obtained by the State of Maine was available for twenty of the points sampled during the field survey program. The sample numbers, radon plus daughter values, and the ratio of the results obtained using the described method compared to Maine's results are shown in Table 6. In a review of the method in use by Maine, it was found that the results of de-emanation analyses should be higher than those obtained by the State of Maine by a factor of 1.95. The average ratio from Table 6 was found to be 3.00.

Table 6

Maine State Health Department Results vs.
Results With De-emanation Method

Sample Designation	Maine* Rn + daughters ($\mu\mu$c/l)	Results of Analysis ($\mu\mu$c/l)	Ratio
1	47,500	34,800	0.73
3	2,550	22,500	10
4	66,000	140,000	2.1
5	1,100	4,660	4.2
7	11,200	40,300	3.6
8	58,000	68,300	1.2
9	15,000	36,700	2.5
13	30,000	75,400	2.5
14	31,000**	78,300	2.5
20	6,592**	14,600	2.2
21	59,250**	139,000	2.4
23	200,000	579,000	2.9
31	35,000	188,000	5.4
32	46,000	120,000	2.6
33	177,500	522,000	2.9
34	5,613**	11,600	2.1
35	19,200	36,600	1.9
39	90,500	204,000**	2.3
			Average = 3.0

*Reference (3)

**Average of two or more determinations

CHAPTER IV

RADON-222 AND LEAD-210 ANALYSIS BY LEAD AND BISMUTH EXTRACTION EMPLOYING DIPHENYLTHIOCARBAZONE

General

Diphenylthiocarbazone, more commonly called dithizone, is a violet-black organic solid which is extensively employed in the colorimetric analysis of trace quantities of certain of the metallic elements. Dithizone is soluble in most common organic solvents, but not in water. The colorimetric analysis of metals is based on the formation of metal-dithizonates which cause a color change of the green dithizone solvent solution. Since dithizonates are not soluble in water, they migrate to the organic solvent and can be removed by solvent extraction. Chloroform and carbon tetrachloride are the most common organic solvents used in the dithizone analysis.

The metals which will form dithizonates are listed in Table 7 along with information about their radioactive isotopes. Most of these metals can be selectively extracted from a solution containing any of the other metals by employing one or more of three techniques. These are: (1) adjustment of the pH of the solution, (2) addition of a complex-forming agent which will tie up other reacting

Table 7

Metals Forming Dithizonates, and Properties of Their Naturally Occurring Radioactive Isotopes*

Metal Forming Dithizonate	Radioactive Isotopes	Source	Type of Decay	Approx. Half-Life
Manganese	---	---	---	---
Iron	---	---	---	---
Cobalt	---	---	---	---
Nickel	---	---	---	---
Copper	---	---	---	---
Zinc	---	---	---	---
Palladium	---	---	---	---
Silver	---	---	---	---
Cadmium	---	---	---	---
Indium	In^{115}	Natural	β	10^{14} yrs.
Tin	Sn^{124}	Natural	double β decay	10^{17} yrs.
Platinum	---	---	---	---
Gold	---	---	---	---
Mercury	---	---	---	---
Thallium	Tl^{206}	Uranium	β	4.19 min.
	Tl^{207}	Actinium	β, γ	4.79 min.
	Tl^{208}	Thorium	β, γ	3.10 min.
	Tl^{210}	Uranium	β	1.32 min.
Lead	Pb^{210}	Uranium	β, γ	22 yrs.
	Pb^{211}	Actinium	β, γ	36.1 min.
	Pb^{212}	Thorium	β, γ	10.6 hr.
	Pb^{214}	Uranium	β, γ	26.8 min.
Bismuth	Bi^{210}	Uranium	α, β	5.02 days
	Bi^{211}	Actinium	α, β, γ	2.16 min.
	Bi^{212}	Thorium	α, β, γ	60.5 min.
	Bi^{214}	Uranium	α, β, γ	19.7 min.

*Metals forming dithizonates according to Sandell (26); radioactive isotopes from Radiological Health Handbook (23).

metals, and (3) alteration of the valence of interfering metals. For a more complete discussion of the techniques for controlling specificity the reader is referred to the text by E. B. Sandell (26).

There was insufficient time in May and June, 1959, to thoroughly test the de-emanation method of radon analysis, presented in Chapter III, before commencement of the sampling program on July 13, 1959. To insure that an adequate method would be available, the colorimetric dithizone analysis for lead was adapted for the radioassays of radon-222 and lead-210 in water. However, since the de-emanation method proved successful for the determination of radon, the dithizone method was primarily developed for the determination of lead-210. The results from the limited application of the method were encouraging, although further work would be necessary for a completely satisfactory method. The data which were obtained are included in this discussion to provide a basis for further development.

Basically, the analysis for radon-222 and lead-210 was performed by extracting lead-214, bismuth-214, lead-210, and bismuth-210 from the water sample with a dithizone-chloroform solution and evaporating the chloroform from a planchet to isolate the radioactive dithizonates. Polonium-214 builds up to equilibrium with bismuth-214 almost instantaneously. The alpha activity from polonium-214 was used to determine the concentration of bismuth-214. Employing

the theoretical decay equations, and making the common assumption of initial equilibrium between radon and its first four daughters, the radon content of the water was determined. The lead-210 concentrations was then found by allowing the lead-214, bismuth-214, and polonium-214 to decay out before recounting the planchet for beta activity. Interference with the radon analysis from polonium-210 was negligible since it was initially absent and grows with a 138-day half-life.

Methodology

The analytical method used is an adaptation of the colorimetric analysis for lead presented in Standard Methods For the Examination of Water and Sewage (27). Several changes were made in procedures and reagent concentrations employed to produce a method suitable for radioassay. The most important of these changes were: (1) the elimination of the steps designed to remove bismuth, (2) an increase in the concentration of the dithizone-chloroform solution, and (3) evaporation of the dithizone-chloroform solution in a planchet to isolate the radioactive materials. The resulting radioassay procedure is described below:

1. Decant a 100-ml sample into a 250-ml separatory funnel.
2. Add 1 ml lead carrier solution and shake for 15 seconds.

3. Add 10 ml sodium citrate solution and shake for 15 seconds.

4. Add 1 ml hydroxylamine hydrochloride solution and shake for 15 seconds.

5. Add 5 drops thymol blue indicator and shake.

6. Adjust to blue color with NH_4OH.

7. Add 5 ml of potassium cyanide solution and shake 15 seconds.

8. Add 5 ml dithizone solution and shake one minute. Drain dithizone into 2" x 5/16" planchet.

9. Repeat the extraction in Step 8.

10. Add 1 ml dithizone solution, shake, and drain into planchet.

11. Evaporate chloroform from planchet below its boiling point.

12. Count planchet for alpha activity after a 30-minute period.

13. Wait about one week and recount for beta activity.

The reagents should be of the following concentrations:

1. Lead Carrier Solution--Dissolve 7.99 mg $Pb(NO_3)_2$ in one liter of distilled water. Concentration is 50 μgm Pb^{++}/ml.

2. Sodium Citrate Solution--Dissolve 10 gm in enough water to make 100 ml of solution.

3. Hydroxylamine Hydrochloride Solution--Dissolve 20 gm in enough water to make 100 ml of solution.

4. Cyanide Solution--Dissolve 10 gm of KCN in water and dilute to 100 ml.

5. Dithizone Solution--Dissolve 50 mg in 100 ml chloroform, (0.05 per cent dithizone in chloroform).

A mixture of pure dithizone in chloroform is green in diluted solution, though it may appear red in reflected light in high dithizone concentrations. The color change, due to the formation of lead and bismuth dithizonates, allows accurate visual determination of the completeness of extraction. Lead dithizonate is red, while bismuth dithizonate is orange-yellow. If the third addition of dithizone solution (1 ml) remains green, all lead and bismuth have been removed from solution. If after the final addition, the solution still deviates from green, further extractions with dithizone must be made. The total quantity (11 ml) of dithizone solution is adequate for a total of about 2.2 mg of lead and bismuth per liter and is governed by the volume of the planchet. A slight increase in total volume of dithizone solution, if necessary, will not cause a great deal of self-absorption if uniform distribution of the residue can be obtained.

Sodium citrate is intended to prevent the precipitation of metal hydroxides into the chloroform layer when the sample is made basic. Hydroxylamine hydrochloride prevents the oxidation of dithizone by ferric iron, an ion common to aerated natural waters. The pH control with NH_4OH is a very important part of the separation process. Clifford and Wichmann (28) have shown that lead is removed completely only between the pH limits of 8.5 to 11. Below pH 6 practically no lead dithizonate is formed, while

above pH 11, the per cent removal falls off slowly. The function of the cyanide solution is to complex several of the dithizonate-producing cations, thus preventing the formation of their dithizonates.

With the use of the above controlling reagents, the dithizonates of only lead, bismuth, tin, and thallium will be formed. Bismuth and lead may be separated from each other by returning the lead to the aqueous phase by shaking with acidified water at pH 3. At this pH, bismuth will remain in the chloroform layer and the lead will move to the aqueous phase. The lead can then be re-extracted from the water. This procedure was not required for this analysis, since bismuth is the first daughter of lead, and produces the desired alpha emitter, polonium-214. Tin and thallium will not interfere with the determination since radioactive tin is a beta emitter with an extremely low specific activity and thallium isotopes, though present in all three natural decay series, are beta emitters with very short half-lives and have no alpha daughters.

Two possibilities exist for serious interference with this method. Lead-212, bismuth-212, and polonium-212 may be present in the water. These isotopes are daughters of radon-220 from the thorium decay series. If thorium isotopes are present, the percentage of radon-220 (thoron) to radon-222 may be calculated by experimentally determining the half-life of the radon-222 daughters analyzed

(lead-214, bismuth-214, and polonium-214) is about 35 minutes compared to the 10.6-hour half-life of the thoron daughters (lead-212, bismuth-212, and polonium-212), a noticeable increase in the experimentally determined half-life will indicate the presence of thoron. If the thoron daughters are absent, or the thoron/radon ratio is a known constant, the radioanalysis following the dithizone extraction may be performed as described above. If, however, interference is significant and variable, a simple modification in the procedure is required for an accurate analysis.

To distinguish alpha activity between polonium-214 and polonium-212, it is necessary to recount the planchet about 5 hours after the initial counting period. During this interval, polonium-214 will decay out while polonium-212 will be present at about 60 per cent of its original concentration. By extrapolating the determined polonium-212 activity back to the time of the first counting period, the relative percentages of both polonium isotopes originally present can be established. These values may then be used to calculate the original radon-222 and radon-220 (thoron) concentrations present at the time of sampling. No interference with the lead-210 radioanalysis will occur if several days are allowed to elapse for the thoron daughter lead-212 (half-life 10.6 hours) to decay out before beta counting.

The second source of error concerns the concentration of calcium and/or magnesium phosphates in the water being analyzed. If either of the metallic elements are present with as much as 5 mg/l phosphate, the complete extraction of lead will not be possible, since $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ are only soluble to a slight extent in ammonical citrate solution and would carry lead down strongly. In complete water analyses, the U. S. Geological Survey (4) found practically no phosphates in nine representative samples from Maine. Therefore, the possibility of interference from this source was considered unlikely. Before employing the dithizone extraction method in another area, the phosphate content of the waters should be examined.

As previously described in Chapter III, the counting equipment available in the field laboratory consisted of a scintillation detection unit and a scaler. For radioassays with the dithizone method, this equipment had to be adapted for alpha scintillation counting of planchets. This was achieved by placing a zinc sulfide-coated Petri dish on the photomultiplier tube and inverting the planchets on the zinc sulfide layer.

Results of Field Work

The de-emanation method for radon analyses produced satisfactory results in the field. Therefore, the dithizone method was employed primarily for the analysis of lead-210.

An attempt was made to determine the counting efficiency of the scintillation detector as adapted to planchet counting, and a number of dithizone analyses for radon-222 were performed for comparison with the results obtained with the de-emanation method.

The determination of the counting efficiency of the equipment was performed by analyzing the radon daughters produced in a sealed ampoule containing a known amount of radium. During the first efficiency determination, five ampoules containing standard radium solutions were broken and each was diluted to 100 ml. The lead and bismuth were extracted immediately, and the alpha activity was determined. A single count was employed on four standards, while the fifth was used to trace a decay curve by a series of counts over a period of several hours. From the trace of the decay curve, it was discovered that the apparent half-life was approximately 50 minutes and that the activity did not die away, but reached a constant plateau. The prolonged half-life was attributed to the relatively high concentration of radium in the solution, which may have been mechanically entrained in the chloroform. A constant increment of alpha activity would thus be produced. The experimental counting efficiencies were 77.0 per cent, 59.8 per cent, 28.3 per cent, 36.2 per cent, and 38.6 per cent for standard solutions containing approximately 10, 100, 1,000, 4,000, and 10,000 $\mu\mu$c radium-226, respectively.

During later attempts at standardization, a modified procedure was used. Three standard radium solutions were analyzed for radon as before with the exception that individual decay curves were determined for all three standards. When the alpha activity became constant, the count rate was recorded as long-life activity and was subtracted from each previous count before plotting the decay curve. The results of this modified method are shown in Fig. 13. The effective half-life of the radon daughters found over the time interval shown was approximately 37 minutes with an efficiency extrapolated to the time of separation of 13 per cent. This half-life closely approximates that expected from theory. It should be noted from Fig. 13 that the alpha activity does not approach a state of logarithmic decay until about one hour after separation. For valid results, samples should be counted after a one-hour decay time so that an accurate correction may be applied to account for decay during the counting interval.

The major portion of the work with this method was for the analysis of lead-210. The radon daughters were extracted as outlined in the section of methodology, page 65, and deposited on planchets. The planchets were then stored to be counted upon return to the laboratory at Georgia Tech. The storage time varied from about one to two months which is more than sufficient time to allow for the complete decay of all beta emitters except lead-210

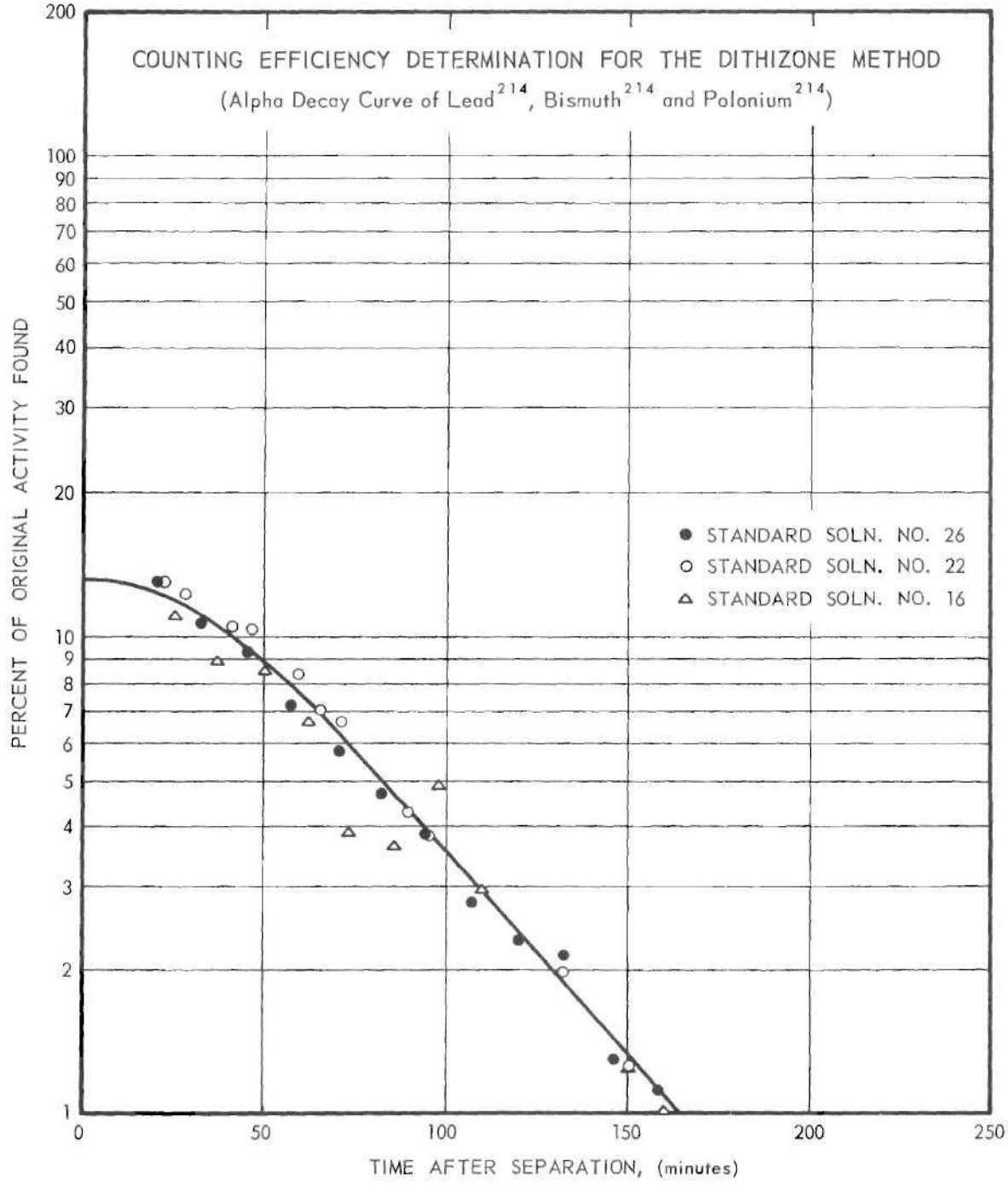


Fig. 13. Counting Efficiency Determination for Dithizone Method

and bismuth-210. No sample was counted at a rate significantly greater than background for either alpha or beta activity. Later attempts to standardize the method with a standard solution of lead-210 produced significant count rates, but the results were inconclusive.

The counting equipment used consisted of an internal proportional counter converter* connected with two scalers** in such a manner as to simultaneously record the alpha-plus-beta activity on one scaler and the alpha activity on the other. Such an arrangement was found to be very economical of time required for the analysis of both the alpha and beta activity of a sample.

One of the major shortcomings of the dithizone method, as presented, lies in the lack of uniform deposition of dithizonates on the planchet upon evaporation. As the remaining chloroform volume reached a thin layer, surface tension pulled the chloroform, with the solids, to the edge of the planchet. Although the solids content in all cases was insufficient to cause significant self-absorption if uniformly distributed over the entire planchet, when

---

*A product of the Nuclear Measurements Corporation, Indianapolis, Indiana, Model PCC-11A.

**Both scalers were produced by the Nuclear-Chicago Corporation, Chicago, Illinois. Alpha activity was recorded on a Model 183A Scaler while alpha-plus-beta activity was recorded on a Model 183B Scaler.

concentrated along the edge an indeterminate and variable amount of self-absorption was obtained. Furthermore, the effective geometry resulting from this distribution is only approximately 25 per cent. The experimentally determined counting efficiency of only 13 per cent shows that self-absorption is significant in the analysis. The effect of non-uniform deposition of solids on the accuracy is illustrated in Table 8 which compares the radon activity found at 19 sampling points by the de-emanation and dithizone methods.

Table 8

Comparison of Radon-222 Concentrations Found by the De-emanation and Dithizone Methods

Sample Designation	De-emanation ($\mu\mu$c/l)	Dithizone ($\mu\mu$c/l)	Sample Designation	De-emanation ($\mu\mu$c/l)	Dithizone ($\mu\mu$c/l)
20	2,900	7,500	99	3,200	7,000
21	27,600	43,000	100	4,320	2,300
22	176,000	120,000	101	1,300	2,600
23	115,000	42,000	102	112,000	50,000
32	23,800	44,000	103	1,610	2,400
33	104,000	44,000	104	9,280	3,100
34	2,320	3,000	105	9,050	9,900
36	6,310	2,900	106	19,200	16,000
51	995	530	107	1,850	1,500
98	2,860	1,500	---	---	---

CHAPTER V

CONCLUSIONS

As a result of the studies for suitable methods for the determination of radon-222, radium-226, and lead-210 in water, the following conclusions were reached:

1. The precipitation, as sulfides, of the lead, bismuth, and polonium daughters of radon-222, with subsequent collection of a millipore filter, produced poor results on certain well waters from Raymond, Maine, because of clogging of the filter paper produced by an unknown precipitate.

2. Verification of radon-222 as the responsible radioisotope was obtained by the repeated counting of four samples from two wells. The experimentally determined half-life of 3.80 days compares favorably with the accepted value of 3.825 days.

3. The efficiency of radon removal from bubblers, by de-emanation, averaged 99.3 per cent when Corning Glass Works' components were used in bubbler construction. The removal efficiency of a second group of bubblers assembled of components produced by Consolidated Glass Works averaged 89.6 per cent. Removal efficiencies were determined with standard solutions in the Corning bubblers, while water

samples were used in the others for routine determinations only.

4. The alpha-counting efficiency of the scintillation detector varied with time due to the photomultiplier tube decay, necessitating frequent measurements and the use of corrections obtained from a graph of counting efficiency versus time.

5. The de-emanation method of radon analysis was reproducible on samples to within ± 9.19 per cent, at 95 per cent confidence, when the time interval between sampling was short.

6. The radon content of a well was found to vary with time within a 95 per cent confidence interval of ± 14.0 per cent; thus, the reproducibility of the method was reduced as determined by successive samples from a single source.

7. The use of air as a de-emanating gas required the use of airborn radon as the background correction factor in the counting rate of the scintillation detector. This elevated the background level to the point that radium analyses were inconclusive.

8. The analysis for radon by radon daughter extraction with diphenylthiocarbazone was not practical as described because of non-uniform deposition of solids and the variable self-absorption which resulted.

CHAPTER VI

RECOMMENDATIONS

The de-emanation method for the analysis of radon-222 and radium-226 can be further improved through a number of modifications as an outcome of these studies.

1. The sensitivity of a photomultiplier tube decays exponentially to a slowly decreasing rate after a period of from one to two months. Therefore, aging of the tube under full operating voltage prior to use in scintillation detection will eliminate the rapid initial decrease in counting efficiency for a given scaler sensitivity. The uncertainty involved in determining the true counting efficiency applicable to the analysis of a given sample will thus be reduced.

2. It is recommended that a supply of a single lot of zinc sulfide be obtained which will be adequate for several months. It was found that one pound of zinc sulfide is sufficient for the preparation of approximately 400 scintillation flasks.

3. The use of a solution of silicone grease in chloroform produced uniform coating of zinc sulfide on the walls of scintillation flasks. However, the silicone grease is very difficult to remove when washing the flasks, requiring special techniques and much time. A substance

which could be removed with a detergent would be of definite advantage. The requirements are only that the materials be sticky enough to hold the zinc sulfide and viscous enough that it will not spread over the individual particles of zinc sulfide and intercept alpha particles.

4. "Pyrex" or other fritted glass discs of uniform porosity are recommended for the fabrication of bubblers. The fritted glass discs produced excellent diffusion of the de-emanating gas and almost complete radon removal from samples. Spring retaining clips should be used on the stopcocks on either end of the bubblers, since the rubber rings, in common use, may cause partial disassembly of the stopcock during transportation. Loose stopcocks will permit the leakage of water from the bubbler and is dangerous in that concentrated nitric acid may also be applied.

5. Some advantage might be gained, especially in the analysis for radium, if the size of the bubblers and scintillation flasks were increased. The size of the scintillation flask is the critical parameter, since above some point the counting efficiency will decrease due to absorption of alpha particles in air before they can reach the walls of the flask. Doubling the size of both the bubblers and scintillation flasks would probably increase reproducibility. A simple twofold increase in bubbler and scintillation flask size would not be sufficient to make

the method practical for radium analysis, since the background counting rate would also be doubled. However, substitution of a radon-free de-emanating gas should produce adequate results. The gas may be air stored to allow radon decay or any other inert gas which will remove radon from solution. The gas should have the smallest molecular weight possible to achieve the maximum effective range of the alpha particles.

6. The dithizone method for radon analysis produced good results except for the non-uniform deposition of solids on the planchet. Uniform distribution might be obtained by using concentric ring planchets, a wetting agent, or a combination of the two. If accurate results could be obtained, the dithizone method would be practical since only ten minutes are required for a separation and special equipment is not required.

APPENDIX A

RECOVERY OF LEAD CARRIER FROM SOLUTION

Table 9

Recovery of Lead Nitrate From Distilled Water Using $(NH_4)_2S$ As Precipitant

Sample No.	Orig. Vol. Of Sol. (ml)	Vol. Of Sol. Used (ml)	Theor. Wt. of Pb Carrier Per Sample Vol. Filtered (gm)	Vol. of $(NH_4)_2S$ Per Liter Of Sample (ml)
1	1000	400	0.0020	10
2	1000	200	0.0020	10
2-A	1000	200	0.0020	10
3	500	500	0.0005	10
4	500	500	0.0010	10
5	500	500	0.0015	10
6	500	500	0.0010	6
7	500	500	0.0010	2

Sample No.	Wt. of Filter Paper (gm)	Wt. of Filter Paper Plus Precip. (gm)	Wt. of Precip. (gm)	Wt. of Pb^{++} In Precip. (gm)	Per cent Pb^{++} Recovery	Time Of Filtration (min)	Remarks
1	0.0143	0.0282	0.0139	0.0120	600	90	Filter Paper dried in 100° C Oven
2	0.0152	0.0288	0.0136	0.0118	590	60	
2-A	0.0243	0.0259	0.0016	0.0014	70	20	
3	0.0243	0.0248	0.0005	0.0004	80	5	
4	0.0284	0.0288	0.0004	0.0003	30	5.5	
5	0.0311	0.0328	0.0017	0.0015	100	120	
6	0.0279	0.0281	0.0002	0.0002	20	5.5	
7	0.0247	0.0246	0.0001	---	---	5.5	

Table 10

Recovery of Lead Carrier From Distilled Water
Using H_2S As Precipitant

Sample No.	Carrier Form (Lead)	Amt. of Carrier Sol. per Liter of Sample (ml)	Wt. of Filter Paper (gm)	Wt. of Filter Paper Plus Precip. (gm)	Wt. of Precip. (gm)
1	Nitrate	1	0.0236	0.0238	0.0002
2	Nitrate	5	0.0289	0.0331	0.0042
3	Nitrate	10	0.0269	0.0368	0.0099
4	Nitrate	20	0.0241	0.0426	0.0185
5	Acetate	0.05	0.0272	0.0275	0.0003
6	Acetate	0.25	0.0241	0.0248	0.0007
7	Acetate	0.5	0.0279	0.0362	0.0083
8	Acetate	1	0.0247	0.0450	0.0203

Sample No.	Theor. Wt. Precip. (gm)	Per cent Pb^{++} Recovery
1	0.0016	12.5
2	0.0058	72.5
3	0.0116	85.3
4	0.0231	80.2
5	0.00099	30.3
6	0.0049	14.3
7	0.0099	83.9
8	0.0197	103

APPENDIX B

DETERMINATION OF THE ABILITY OF AMMONIA TO INCREASE THE PRECIPITATION OF LEAD WITH H_2S

Determination of the Ability of Ammonia To Increase the Precipitation of Lead with H_2S

Procedure

1. Add 8.5 ml concentrated HCl to 1 liter of distilled water in a dust-free 1500 ml beaker.
2. Add 5 mg Pb++ as $Pb(NO_3)_2$
3. Bubble H_2S through solution for 5 minutes.
4. Filter through millipore type HA filter, weighing before and after to determine the per cent of lead recovery. Dry filter paper for 10 minutes on a hotplate before each weighing.

Variables

#1	Beaker No. 1	Follow above procedure.
#2	Beaker No. 2	Add 1 cc NH_4 immediately following H_2S addition.
#3	Beaker No. 3	Add 5 cc $(NH_4)_2S$ after H_2S addition.
#4	Beaker No. 4	Add 5 cc $(NH_4)_2S$ at step #1 and eliminate step #3.
#5	Beaker No. 5	Repeat as in #2.

Results

(Times in Parentheses are Filtration Times)

#1 wt. paper after filtering 30.5 mg
wt. paper before filtering 26.1 mg

wt. PbS = 4.4 mg

% Recovery = $\frac{4.4}{5.8}$ x 100 = 76% (20 min.)

#2 wt. paper after filtering 29.4 mg
wt. paper before filtering 24.0 mg

wt. PbS = 5.4 mg

$\%\ \text{Recovery} = \frac{5.4}{5.8} \times 100 = 93\%$ (15 min.)

#3 wt. paper after filtering 39.6 mg
wt. paper before filtering 26.7 mg

wt. PbS = 13.9 mg

$\%\ \text{Recovery} = \frac{13.9}{5.8} \times 100 = 240\%$ (39 min.)

#4 Filtration prevented by clogging

#5 wt. paper after filtering 31.8 mg
wt. paper before filtering 26.7 mg

wt. PbS = 5.1 mg

$\text{A Recovery} = \frac{5.1}{5.8} \times 100 = 88\%$ (13 min.)

Summary

Average per cent of recovery #2 and #5 = 90.5 per cent.

Increase in recovery over #1 = 14.5 per cent.

APPENDIX C

SAMPLE LOCATIONS CORRESPONDING TO THE SAMPLE DESIGNATIONS IN THE TEXT

Sample Locations

Sample Number	Location
1	L. H. Bradway Lumber Company Windham, Maine
3	Raymond Water Company Raymond, Maine
4	B. A. Mann Raymond, Maine
5	Vincent Clark Raymond, Maine
7	Donald Van Dusen Raymond, Maine
8	Dodge Raymond, Maine
9	George Henry Raymond, Maine
11	Winant Raymond, Maine
13	T. Kinnelly Raymond, Maine
14	Pine Hollow Lodge Raymond, Maine
20	Portland Pipeline Co., (Pumping Station) Raymond, Maine
21	Portland Pipeline Co., (Superintendent's Cottage) Raymond, Maine
22	Dielectric Products Engineering Company, Inc. Raymond, Maine
23	Charles Harmon Raymond, Maine

Sample Number	Location
31	E. R. Clough's Grocery Store Raymond, Maine
32	Harold Bishop Raymond, Maine
33	Rev. Emily Pitcock Raymond, Maine
34	Charles Small Raymond, Maine
35	Raymond Town Hall Raymond, Maine
36	J. O. Small Raymond, Maine
39	Dr. Charles D. Brown Raymond, Maine
51	Name Unknown Raymond, Maine
98	Dillingham Naples, Maine

APPENDIX D

RADIUM STANDARDS

Radium Standards Available In the Field

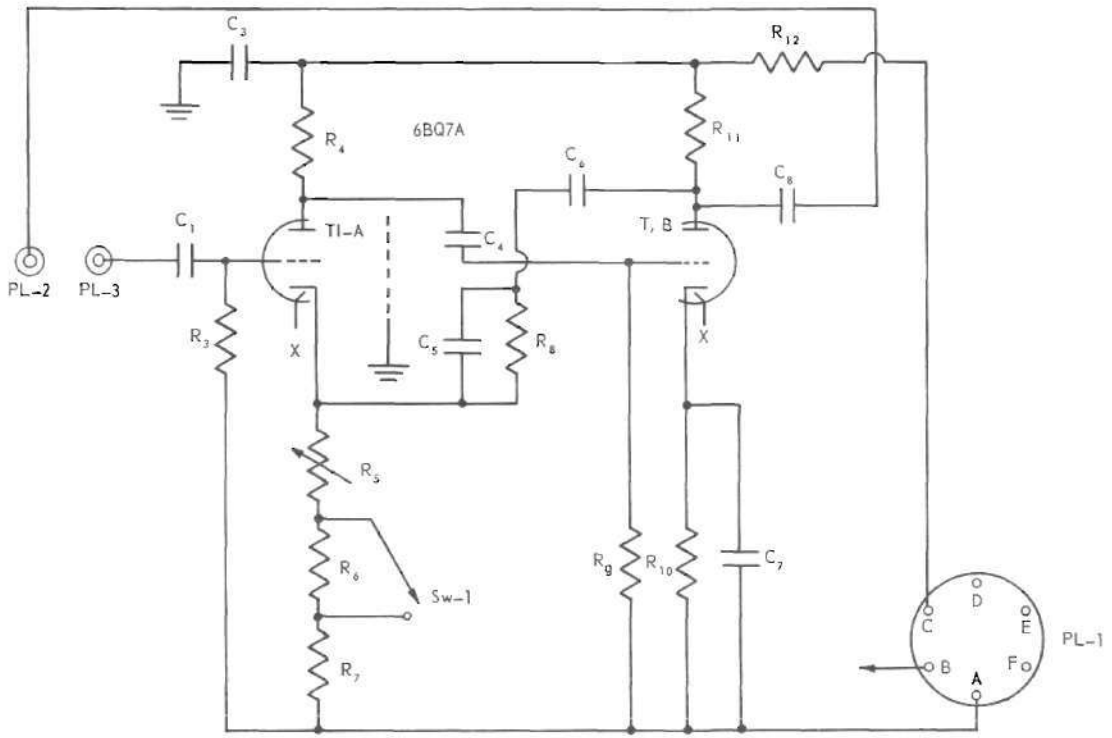
Std. No.	Wt. of Std. Sln. (gm)	Volume of Std. Sln. (ml)	Conc. of Std. Sln. ($\mu\mu$c Ra^{226}/ml)	Total Activity of Std. ($\mu\mu$c)	Date & Time of Sealing
1	5.104	5.123	2	10.246	7/3/59 7:00 PM
2	5.111	5.130	2	10.260	7/3/59 7:00 PM
3	5.118	5.137	2	10.274	7/3/59 7:00 PM
4	5.124	5.143	2	10.286	7/3/59 7:00 PM
5	5.119	5.138	2	10.276	7/3/59 7:00 PM
11	5.110	5.129	20	102.58	7/3/59 7:00 PM
12	5.113	5.132	20	102.64	7/3/59 7:00 PM
13	5.165	5.184	20	103.68	7/3/59 7:00 PM
14	5.151	5.170	20	103.40	7/3/59 7:00 PM
15	5.141	5.160	20	103.20	7/3/59 7:00 PM
21	5.100	5.119	200	1023.8	7/3/59 8:00 PM
22	5.098	5.117	200	1023.4	7/3/59 8:00 PM
23	5.138	5.157	200	1031.4	7/3/59 8:00 PM
24	5.162	5.181	200	1036.2	7/3/59 8:00 PM
25	5.156	5.175	200	1035.0	7/4/59 2:00 AM
31	1.998	2.005	2000	4010.0	7/3/59 8:00 PM
32	2.085	2.093	2000	4186.0	7/3/59 8:00 PM
33	2.072	2.080	2000	4160.0	7/3/59 8:00 PM
34	2.044	2.052	2000	4118.0	7/3/59 8:00 PM
35	2.051	2.059	2000	4118.0	7/3/59 8:00 PM
41	5.168	5.187	2000	10374	7/4/59 2:00 AM
42	5.169	5.188	2000	10376	7/4/59 2:00 AM
43	5.147	5.166	2000	10332	7/4/59 2:00 AM
44	5.162	5.181	2000	10362	7/4/59 2:00 AM
45	5.151	5.170	2000	10340	7/4/59 2:00 AM

APPENDIX E

CIRCUIT DIAGRAMS OF SCINTILLATION DETECTOR COMPONENTS

PARTS LIST FOR PERAMPLIFIER

PL-2 & PL-3	2	AMPHENOL COAX. CONNECTORS
C_3 & C_6	2	4 μfd AT 480 V
R_4 & R_{11}	2	10 K AT 1 W RESISTOR
C_4 & C_5	2	100 μμfd AT 600 V
R_5 & R_6	2	1 K AT 1/2 W
R_3 & R_9	2	470 K AT 1/2 W
PL-1	1	14S-6S AMPHENOL CONNECTOR
R_7	1	220 OHM AT 1/2 W
C_7	1	.1 AT 600 V
R_5	1	1 K AT 2 W POT
S_1	1	SPST SWITCH
C_8	1	.001 AT 6 KV
C_1	1	500 μμfd AT 20 KV
	1	9 PIN VECTOR SOCKET
T_1	1	6BQ7A TUBE
	1	BUD MINIBOX
R_{12}	1	1 K AT W RESISTOR
R_{10}	1	220 OHM RESISTOR

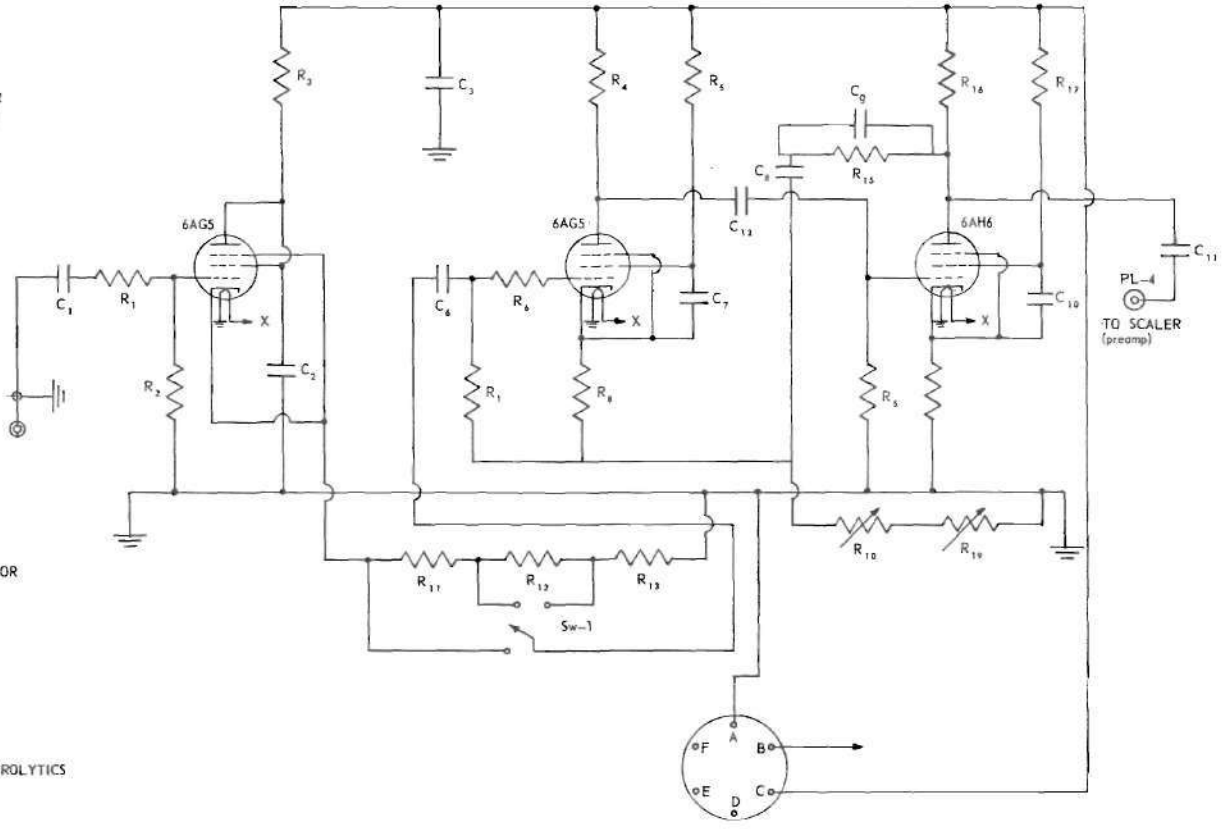


SCHEMATIC DIAGRAM OF PREAMPLIFIER IN SCINTILLATION DETECTOR

Fig. 14.

PARTS LIST FOR AMPLIFIER-DISCRIMINATOR

PL-1; PL-2	2	145 6S AMPHENOL CONNECTOR
PL-3; PL-4	2	STANDARD COAX CONNECTOR
C_1	1	75 $\mu\mu$fd CERAMIC
C_9	1	15 $\mu\mu$fd CERAMIC
R_5; R_9; R_{17}	3	100 K AT 1 W RESISTOR
R_8; R_{11}	2	330 OHM AT 1/2 W RESISTOR
R_2	1	10 MEG AT 1/2 W RESISTOR
C_2; C_6; C_3; C_{12}; C_7; C_{10}	8	.01 μfd 600 V (2 EXTRA)
R_3	1	47 K 1/2 1 W RESISTOR
R_{15}	1	3.6 K 1/2 1 W RESISTOR
R_{16}	1	22 K AT 1 W RESISTOR
R_4	1	1.5 K AT 1 W RESISTOR
R_7	1	1 MEG AT 1/2 W RESISTOR
R_6	1	220 OHM AT 1/2 W RESISTOR
C_8	1	.05 AT 600 V
R_{10}	1	470 OHM AT 1/2 W
R_{18}	1	1 K AT 2 W POT
R_{19}	1	100 OHM AT 1 W POT
R_{11}	1	2.7 K AT 1 W 5% RESISTOR
R_{12}	1	270 OHM AT 1/2 W 5% RESISTOR
R_{13}	1	30 OHM AT 1/2 W RESISTOR
Sw-1	1	4 POSITION ROTARY SW
	1	6AH6
	3	7 PIN MIN SOCKETS
	2	6AG5
C_{11}	1	.01 AT 6 KV
	6	6 TERMINAL TERM STRIPS
C_4; C_5	2	40-40 μfd AT 400 WVDC ELECTROLYTICS
R_{14}	1	3600 OHM 1/2 W RESISTOR

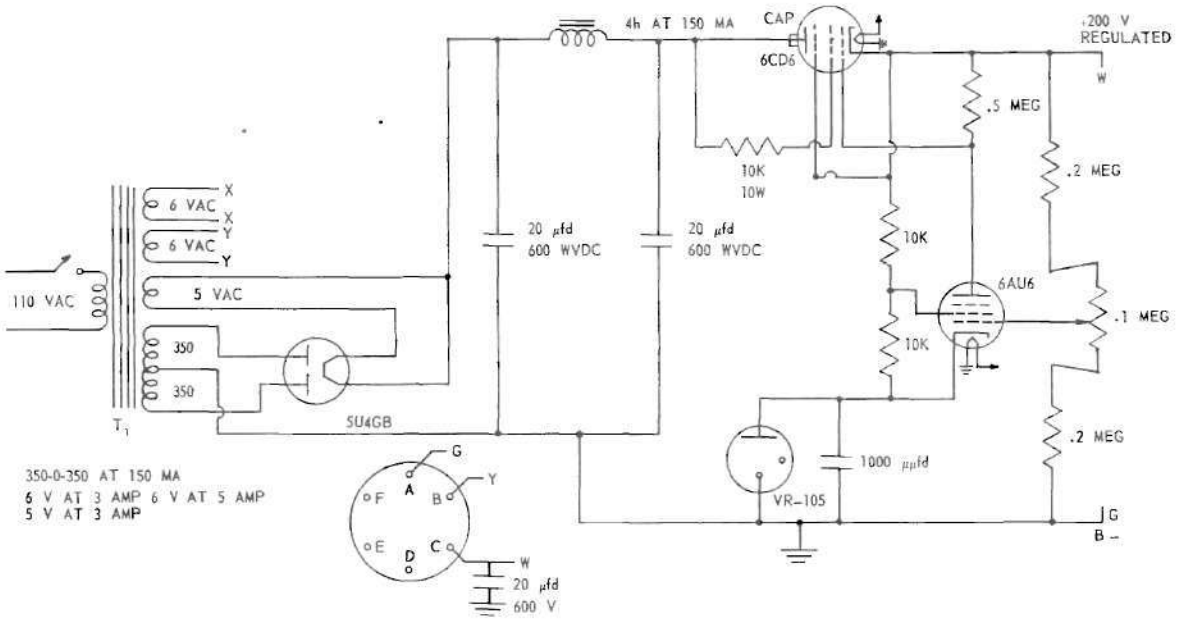


SCHEMATIC DIAGRAM OF AMPLIFIER-DISCRIMINATOR IN SCINTILLATION DETECTOR

Fig. 15.

PARTS LIST FOR LOW-VOLTAGE POWER SUPPLY

3	20 μfd AT 600 V
1	350-0-350 AT 150 MA XFMR W FILIAMENT TAPS
1	5U4CB
1	6AU6
1	6CD6G
1	CHASIS BASE
1	CHASSIS BOTTOM PLATE
1	14S-6S AMPHENOL CONNECTOR
1	LINE CORD
1	SPST TOGGLE
3	OCTAL SOCKETS
1	7 PIN MINIATURE SOCKET
1	1000 μμfd CERAMIC
2	10 K AT 1 W RESISTOR
1	.5 MEG AT 1/2 W RESISTOR
2	.2 MEG AT 1/2 W RESISTOR
1	.1 MEG POT
1	4 HY AT 150 MA CHOKE



SCHEMATIC DIAGRAM OF LOW-VOLTAGE POWER SUPPLY IN SCINTILLATION DETECTOR

Fig. 16.

APPENDIX F

TYPICAL CALCULATION OF RADON ACTIVITY WITH FIELD AND LABORATORY DATA SHEETS

Sample Calculations

The illustration of the calculations involved in determining the radon activity of a sample may best be performed by following a typical calculation step by step. Typical field data and calculation sheets used for both radon and radium are shown on pages 99 and 100.

The field data sheet is filled out at the time of sample collection. Of the data shown, only items 1, 2, 11, 12, and 13 are of direct importance in the analysis. The sample designation, bubbler number, and time and date of radon separation are transferred to the laboratory data sheet and the sample is counted, providing the information in items 6-13. Calculation involves applying corrections for (1) radon removal efficiency, (2) counting efficiency, (3) state of daughter equilibrium, and (4) water sample volume.

Item 13 is the gross cpm (counts per minute) minus the background cpm or item 10 minus item 11. Correction for incomplete removal is made in item 15 by dividing item 13 by item 14, which, for this analysis, is either 0.993 or 0.896, depending on the bubbler number. Correction is then made for efficiency by dividing item 15 by item 16 where item 16 is the counting efficiency from Fig. 7. Item 18 is the ratio of the total alpha activity to the initial radon activity, from Fig. 3, and is used to

Sampling Date 8/19/59

FIELD DATA SHEET

1) Sample Designation	3
2) Location of Sampling Point	Raymond Water Co. Raymond, Maine
3) Depth of Well	30'
4) Type of Well	dug
5) Use of Well	commercial & domestic
6) Date Well First Used	?
7) Number of Persons Using Well	12 families
8) Ages of Persons Using Well	?
9) Location of Well at Sampling Point	---
10) Collection Point Within Water System	upstairs kitchen faucet
De-emanation Method	
11) Bubbler Number	18
12) Time of Sample Collection	5:08 PM
13) Time of Radon Separation	5:10 PM
Dithizone Method	
14) Collection Bottle Number	8
15) Time of Sample Collection	5:10 PM
16) Time of Radon Daughter Separation	---
Remarks	

Sampling Date 8/19/59

LABORATORY DATA SHEET--RADON AND RADIUM IN WATER

	RADON	RADIUM
1) Sample designation	3	3
2) Bubbler number	18	18
3) Time & date of storage		10:00 AM 8/20
4) Time & date of Rn separation	5:10 PM 8/19	2:42 PM 8/27
5) Time for Rn buildup from Ra (days)		
6) Time and date of beginning of count	4:36 PM 8/20	1:00 AM 8/29
7) Time for Rn + daughter decay (min.)	1406	2062
8) Total alpha counts	5,120	170
9) Duration of count (min.)	20.00	30.00
10) C.P.M. (#8/#9)	256.0	5.67
11) Background (cpm)	0.4	2.00
12) Duration of background count	5 min.	30 min.
13) C.P.M. (#10-#11)	255.6	3.67
14) Rn removal efficiency (%/100)	0.896	0.896
15) C.P.M. (#13/#14)	285	4.09
16) Counting efficiency (%/100)	0.550	0.689
17) C.P.M. (#15/#16)	518	5.94
18) Count ratio from decay curve (%/100)	2.53	2.32
19) D.P.M. (#17/#18)	205	2.56
20) % Rn buildup from Ra (%/100)		0.729
21) D.P.M. of Ra (#19/#20)		3.51
22) Sample volume (ml)	20.6	20.6
23) D.P.M./l (#19 or #21 x 1000/#22)	9,950	170
24) $\mu\mu$/l (#23/2.22)	4,480	76.6
25) Remarks		

determine the dpm (disintegrations per minute) of the sample by dividing item 18 into item 17. Item 19 is then divided by item 22 (sample volume) and multiplied by 1000 to obtain the true dpm/l of the sample. Division by 2.22 then produces the activity of the sample in $\mu\mu$c/l. The activity obtained is that of radon-222 alone, but may be converted to the more common radon plus daughters by multiplying by 5.025.

APPENDIX G

THE APPROXIMATE ALPHA ACTIVITY OF AIR AT TYPICAL SAMPLING POINTS

The Approximate Alpha Activity of Air at Typical Sampling Points

Sampling Point*	Alpha Activity of Air ($\mu\mu$c/l)
1	1.0
3	0.2
4	0.6
5	0.8
7	13.2
8	0.8
9	1.1
11	0.5
13	12.0
14	0.9
20	20.3
21	49.9
22	24.9
23	4.0
31	1.1
32	49.1
33	2.0
34	0.9
35	18.5
36	1.5
39	2.1
51	2.3
98	3.4
	Average = 9.2

*See Appendix C for location

APPENDIX H

STATISTICAL ANALYSES FOR THE REPRODUCIBILITY OF THE DE-EMANATION METHOD

Table 11

Statistical Analysis for the Reproducibility
of the De-emanation Method on Standard Solutions

Standard Number	Counting Effic.	Ave. Counting Efficiency of Group	Dev. From Average	Per Cent Dev. From Ave.	(Per Cent Dev.)^2
1	68.5	71.08	2.58	3.63	13.17
2	73.4	71.08	2.32	3.26	10.63
31	73.9	71.08	2.82	3.97	15.76
32	68.5	71.08	2.58	3.63	13.18
1	61.4	62.55	1.15	1.84	3.39
2	61.4	62.55	1.15	1.84	3.39
31	66.1	62.55	4.55	5.66	32.04
32	61.3	62.55	1.25	2.00	4.00
1	52.5	56.23	3.73	6.63	43.96
2	54.9	56.23	1.33	2.37	5.62
31	56.7	56.23	0.47	0.84	0.71
32	60.8	56.23	4.57	8.13	66.10
1	70.7	68.38	2.32	3.39	11.49
2	74.5	68.38	6.12	8.95	80.10
23	62.5	68.38	5.88	8.60	73.96
31	65.6	68.38	2.78	4.07	16.56
32	68.6	68.38	0.22	0.32	0.10
1	61.7	63.30	1.60	2.53	64.01
2	63.2	63.30	0.10	0.16	0.03
23	67.4	63.30	4.10	6.48	41.99
31	59.7	63.30	3.60	5.69	32.38
32	64.5	63.30	1.20	1.90	3.61
				$\Sigma = 85.89$	$\Sigma = 536.3$

All Standards

Average Deviation (A. D.) $= \frac{85.89}{22} = 3.90\%$

Standard Deviation (σ) $= \sqrt{\frac{563.3}{21}} = 26.82 = 5.18\%$

95% Confidence Interval $= 1.96\,\sigma = \pm 10.2\%$

$$\frac{\sigma}{\text{A.D.}} = \frac{5.18}{3.90} = 1.33$$

Low Activity Standards (1 & 2)

(Per Cent Deviation) = 34.60

$(\text{Per Cent Deviation})^2 = 235.8$

$$\text{A. D.} = \frac{34.60}{10} = 3.46\%$$

$$\sigma = \sqrt{\frac{235.8}{9}} = 26.20 = 5.12\%$$

$$\frac{\sigma}{\text{A.D.}} = 1.48$$

95% Confidence Interval $= \pm 10.0\%$

High Activity Standards (31 & 32)

(Per Cent Deviation) = 36.21

$(\text{Per Cent Deviation})^2 = 184.4$

$\text{Average Deviation} = \frac{36.21}{10} = 3.62\%$

$\text{Standard Deviation} = \sqrt{\frac{184.4}{9}} = 20.49 = 4.53\%$

$\frac{\sigma}{\text{A.D.}} = 1.25$

95% Confidence Interval = $\pm$ 8.88%

Table 12

Statistical Analysis of the
Reproducibility of Triplicate Samples

Sample No.	Activity ($\mu\mu$c/l)	Group Average Activity ($\mu\mu$c/l)	Dev. From Group Ave.	Per Cent Deviation	(Per Cent Dev.)^2
39A	44,700	45,800	1,100	2.40	5.76
39B	45,900	45,800	100	0.22	0.05
39C	46,800	45,800	1,000	2.18	4.75
39D	21,700	19,930	1,770	8.88	78.85
39E	19,000	19,930	930	4.66	21.72
39F	19,100	19,930	830	4.16	17.31
39G	36,800	37,600	1,200	3.19	10.18
39H	37,600	37,600	0	0	0.00
39I	38,400	37,600	1,200	3.19	10.18
39J	2,430	2,347	83	3.54	12.53
39K	2,360	2,347	13	0.55	0.30
39L	2,250	2,347	97	4.13	17.06
143A	6,800	6,127	673	10.98	120.56
143B	6,080	6,127	47	0.77	0.59
143C	5,500	6,127	627	10.23	104.65
143D	17,500	16,900	600	3.55	12.60
143E	15,700	16,900	1,200	7.10	50.41
143F	17,500	16,900	600	3.55	12.60
143G	14,800	14,070	730	5.19	26.94
143H	14,200	14,070	130	0.92	0.85
143I	13,200	14,070	870	6.18	38.19
143J	12,900	13,870	970	6.99	48.86
143K	14,200	13,870	330	2.38	5.66
143L	14,500	13,870	630	4.54	20.61
143M	13,600	13,530	70	0.52	0.27
143N	13,500	13,530	30	0.22	0.05
1430	13,500	13,530	30	0.22	0.05
				Σ = 100.44	Σ = 571.3

Average Deviation (A.D.) $= \frac{100.44}{27} = 3.72\%$

Stand. Deviation (σ) $= \sqrt{\frac{571.3}{26}} = 4.69\%$

$\frac{\sigma}{\text{A.D.}} = \frac{4.69}{3.72} = 1.26$

95% Confidence Interval $= \pm$ 9.19%

Table 13

Statistical Analysis of Repeated Samples From Sampling Point No. 39

Activity ($\mu\mu$c/l)	Deviation	Per Cent Deviation	(Per Cent Deviation)^2
197,000	23,700	10.74	115.35
211,000	9,700	4.40	19.36
210,000	10,700	4.85	23.52
233,000	12,300	5.57	31.02
208,000	12,700	5.75	33.06
242,000	21,300	9.65	93.12
203,000	17,700	8.02	64.32
258,000	37,300	16.90	285.61
235,000	14,300	6.48	41.99
220,000	700	0.32	0.10
211,000	9,700	4.40	19.36
Σ = 2,424,700		Σ = 77.08	Σ = 726.8

$$\text{Average Activity} = \frac{2,427,700}{11} = 220,700$$

$$\text{Average Deviation (A.D.)} = \frac{77.08}{11} = 7.01\%$$

$$\text{Standard Deviation} = \sqrt{\frac{726.8}{10}} = 8.53\%$$

$$\frac{\sigma}{\text{A.D.}} = 1.22$$

95% Confidence Interval = $\pm$ 16.7%

BIBLIOGRAPHY

1. Love, S. K., "Natural Radioactivity of Water," Industrial and Engineering Chemistry, Vol. 43, No. 7, 1951, p. 1541.

2. Smith, Benjamin, M., Natural Radioactivity In Maine And New Hampshire Ground Water Supplies, Unpublished M. S. Thesis, Georgia Institute of Technology, 1960.

3. Van der Smissen, E. and Weiss, E. S., Interim Report on Radioactivity in Deep-Well Waters, Raymond, Maine, Research Branch, Division of Radiological Health, U.S.P.H.S., November, 1958.

4. Barker, F. B., Research Chemist, U. S. Geological Survey, Federal Center, Denver, Colorado, Personnal communication to Dr. W. N. Grune, Professor of Civil Engineering, Georgia Institute of Technology, March 31, 1959.

5. Butler, Arthur P., Jr., "The Geological Survey's Work On The Geology of Uranium and Thorium Deposits," U. S. Geological Survey, TEI-207, April, 1952.

6. Hursh, John B., "The Radium Content of Public Waters Supplies," The University of Rochester, Atomic Energy Project, UR-257, Contract W-7401-eng-49, May 5, 1953.

7. Kuroda, P. K., and Yokayama, Yuji, "Determination of the Short-Lived Decay Products of Radon in Natural Waters," Analytical Chemistry, Vol. 26, Part 2, 1954, p. 1509.

8. Rogers, Allen S., "Physical Behavior and Geologic Control of Radon in Mountain Streams," U. S. Geologic Survey Bulletin 1052-E, 1958.

9. "Regulation of Radiation Exposure By Legislative Means," National Bureau of Standards, N. B. S. Handbook 61, U. S. Government Printing Office, Washington, D. C., December 9, 1955.

10. Rieck, H. G. and Perkins, R. W., "Radium Determinations in Soil, Vegetation and Water by Radon Counting," Biophysics Section, Radiological Sciences Department, Hanford Atomic Products Operation, General Electric Corporation, AEC Contract No. W-31-109-eng-52, HW-32210 Rev., 1956.

11. Hudgens, J. E., Benzing, R. O., Cali, J. P., Meyer, R. C., and Nelson, L. C., "The Determination of Radium or Radon In Gases, Liquids, or Solids," New Brunswick Laboratory, United States Atomic Energy Commission, NYO-2010, May 10, 1950.

12. Jenkins, E. N., and Sneddon, G. W., "The Monitoring of Effluent for Alpha Emitters, Part 3. Radium," Atomic Energy Research Establishment, Harwell, Berkshire, Research Group, United Kingdom Atomic Energy Authority, AERE CIR 2385, 1958.

13. Russell, E.R., Lesko, R. C., and Schubert, J., Nucleonics, Vol. 7, No. 1, 1950, p. 60.

14. Ames, D. P., Sedlet, J., Anderson, H. H., Kohman, T. P., "The Transuranium Elements," National Nuclear Energy Series, IV-14B, G. T. Seaborg, J. J. Katz, W. M. Manning, editors, New York, 1949, pp. 1700-16.

15. Harley, J. H. and Foti, S., "Determination of Micro-microgram Quantities of Radium," Nucleonics, Vol. 10, No. 2, 1952, pp. 45-47.

16. Barker, F. B. and Thatcher, L. L., "Modified Determination of Radium in Water," Analytical Chemistry, Vol. 29, 1957, p. 1573.

17. Thorburn, R. C. and Healy, J. W., "A Rapid Simple Method For the Determination of the Radon Content of Water," Development Div., Health Instruments Div., Hanford Works, Richland, Wash., H. W.-18321, 1950.

18. Fresco, J., Hardy, E., and Harley, J. H., "A Method For The Determination of Radon in Water," Health and Safety Laboratory, New York Operations Office, U. S. Atomic Energy Commission, NYO-4664, November, 1955.

19. Holaday, D. A., Rushing, D. E., Coleman, R. C., Woolrich, P. F., Kusnetz, H. L., and Bale, Wm. F., "Control of Radon and Daughters (In Uranium Mines and Calculations on Biological Effects)," Department of Health, Education and Welfare, Public Health Service, Publications No. 494, U. S. Government Printing Office, 1957.

20. Rushing, D. E., Principal Chemist, Occupation Health Field Station, Salt Lake City, Utah, Personal Communication to Dr. Werner N. Grune, May 15, 1959.

21. Hodgman, Charles D., ed. in chief, "Solubilities of Various Gases in Water," Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, Ohio, 1954, p. 1611.

22. Rutherford, E., Chadwick, J., and Ellis, C. D., Radiations From Radioactive Substances, Cambridge University Press, London, 1951, p. 13.

23. Kinsman, S., Anderson, F. D., Cleveland, F. D., Harless, B. L., Henke, C. F., Radiological Health Handbook, Bureau of State Services, Public Health Service, U. S. Government Printing Office, Washington, 25, D. C., 1957.

24. Harris, W. B., LeVine, H. D., and Watnick, S. I., "Portable Radon Detector for Continuous Air Monitoring," A. M. A. Archives of Industrial Health, Vol. 16, 1957, pp. 493-498.

25. Croxton, F. E. and Cowden, D. J., Applied General Statistics, New York, 1939.

26. Sandell, E. B., Colorimetric Determination of Traces of Metals, 2nd Ed., Interscience Publishers, Inc., New York, 1950.

27. Standard Methods for the Examination of Water and Sewage, 10th Ed., American Public Health Association, 1955.

28. Clifford, P. A. and Wichmann, H. J., "Dithizone Methods for the Determination of Lead," Journal of the Association of Official Agricultural Chemists, Vol. 19, 1936, p. 134.